ANALYTICAL ABSTRACTS

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

322. **Iodoxine as a new analytical reagent.** A. K. Mukherjee and B. Banerjee (*Naturwissenschaften*, 1955, **42** [14], 416–417).—Iodoxine (8-hydroxy-5:7-di-iodoquinoline) reacts with different metal ions in solution to give characteristic colours and ppt. The reagent is fairly soluble in pyridine and dioxan. A 1 to 2 per cent. solution of iodoxine in dioxan was used to investigate the ppt. and colour reactions with various metal ions (a pyridine solution of the reagent behaves similarly). The colours of the ppt. are as follows—$Cu^{\cdot\cdot}$ greenish yellow, $Ni^{\cdot\cdot}$ red-brown, $Co^{\cdot\cdot}$ chocolate brown, $Fe^{\cdot\cdot\cdot}$ greenish grey, $VO_2^{\cdot\cdot}$ orange-red, $Pd^{\cdot\cdot}$ orange-yellow, $Th^{\cdot\cdot\cdot\cdot}$ orange-yellow, $Zr^{\cdot\cdot\cdot\cdot}$ cream-yellow, $Ti^{\cdot\cdot\cdot\cdot}$ pink-yellow, $VO_2^{\prime}$ pale yellow, and $Pb^{\cdot\cdot}$ yellow. The reagent reacts quant. with Cu, Ni, Fe, Zr, Th, U, V and Ti at different pH values. A ppt. is obtained with a soln. containing 0·4 mg of $Fe^{\cdot\cdot\cdot}$ in 200 ml, and with a soln. containing 0·2 mg of the ions of Zr, Th, U and Cu in 20 ml. The ppt. of Cu can be weighed directly, after being dried at 110° to 120° C. The reagent is suitable for the colorimetric determination of Fe and V.

S. NEUBERGER

323. **The application of thio salts in analysis. III. A new scheme of qualitative analysis. Part C.** I. K. Taimni and G. B. S. Salaria (Univ. of Allahabad, India) (*Anal. Chim. Acta*, 1955, **13** [3], 205–209).—The original scheme proposed (*Anal. Abstr.*, 1954, **1**, 219) has been improved and modified as follows: (*i*) the metals are pptd. with *N* Na_2S instead of conc. ammonium sulphide, (*ii*) aq. Na_2CO_3 is added with Na_2S in order to ppt. Ba, Ca and Sr with the sulphides and hydroxides, (*iii*) the lengthy separation of Ce and Th from the iron group is eliminated by testing for these two elements within that group, (*iv*) Tl is completely pptd. with the copper group by the addition of KI in the treatment with *N* HCl, and (*v*) new tests for the detection of Ni, Te and Au are substituted.

W. J. BAKER

324. **Replacement of hydrogen sulphide and ammonium sulphide in qualitative analysis by thioacetamide.** W. F. Bon (*Chem. Weekbl.*, 1955, **51** [39], 677–678).—This is a criticism of a paper by Bloemendal and Veerkamp (*Ibid.*, 1953, **49**, 147) recommending the replacement of H_2S and $(NH_4)_2S$ by thioacetamide.

P. HAAS

325. **Volumetric studies in oxidation-reduction reactions. III. Reduction with ferrous ethylenediamine sulphate. Indirect determinations.** B. Singh and S. Singh (Punjab Univ. Coll., Hoshiarpur, India) (*Anal. Chim. Acta*, 1955, **13** [3], 222–225).—Ferrous ethylenediamine sulphate (**I**) can be used as a reducing agent in acid medium for the indirect volumetric determination of $KClO_3$, $KBrO_3$, $KMnO_4$, KIO_4, $K_2Cr_2O_7$, $K_2S_2O_8$, $K_3Fe(CN)_6$, H_2O_2 and $Ce(SO_4)_2$. An excess of a 0·05 *N* solution of **I** is added to the sample in the presence of 1 to 2 *N* H_2SO_4, and the unused **I** is titrated with 0·05 *N* $KMnO_4$ or $K_2Cr_2O_7$. Slight modifications for certain of the above-mentioned compounds are described; for $KBrO_3$ and KIO_4 the titration should be made with $K_2Cr_2O_7$ soln. The accuracy is good.

W. J. BAKER

326. **Potentiometric studies in oxidation-reduction reactions. XX. Reduction with ferrous ethylenediamine sulphate. Indirect determinations.** B. Singh, S. Singh and H. Singh (Punjab Univ. Coll., Hoshiarpur, India) (*Anal. Chim. Acta*, 1955, **13** [3], 288–292).—The determination of $K_2Cr_2O_7$, H_2O_2, $KMnO_4$, $K_2S_2O_8$, $KClO_3$, $KBrO_3$ or $Ce(SO_4)_2$ can be made indirectly by reduction of each compound with excess of 0·05 *N* ferrous ethylenediamine sulphate (**I**) in conc. H_2SO_4 soln., followed by potentiometric titration of the excess of **I** with 0·05 *N* $KMnO_4$. Platinum foil is used as an oxidation-reduction electrode coupled with a S.C.E. through an agar-KCl bridge. Precautions to be taken and some results obtained are listed.

W. J. BAKER

327. **Reduction in an alkaline solution by the use of liquid zinc amalgam. (Metallic reducing agents in analytical chemistry.)** Chozo Yoshimura (*J. Chem. Soc. Japan, Pure Chem Sect.*, 1955, **76** [4], 411–413).—Quinquevalent Sb is readily reduced (3 min.) to $Sb^{\cdot\cdot}$ with zinc amalgam in 2 *N* KOH in the presence of $Na_4P_2O_7$. A small amount of tartaric acid is added to the product, which is titrated with standard $KBrO_3$ soln., with indigo carmine as indicator. In a less alkaline soln. (*e.g.*, at pH 8) the reduction with Zn-Hg is much slower. Uranate, vanadate and molybdate are reduced with Zn-Hg in a weakly alkaline soln. containing $NaHCO_3$ and $Na_4P_2O_7$, and titrated with $KMnO_4$ (U and V) or $KBrO_3$ (Mo); indigo carmine is used as indicator.

K. SAITO

328. **The use of metallic antimony and nickel as reducing agents. (Metallic reducing agents in analytical chemistry.)** Chozo Yoshimura (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [4], 409–411).—Antimony dust is a very weak reducing agent in acidic soln. and can be used only in conjunction with heating. The ions of Fe^{III} and Sn^{IV} are reduced with Sb in 3 to 6 *N* HCl or H_2SO_4 and can then be titrated with $Ce^{\cdot\cdot\cdot\cdot}$ soln. When $Ti^{\cdot\cdot\cdot\cdot}$ are reduced with Sb in 10 *N* H_2SO_4, $Ti^{\cdot\cdot\cdot}$ can be titrated with methylene blue without removing the excess of Sb. The ions of U^{VI} and W^{VI} are also capable of being reduced with Sb in 6 *N* H_2SO_4 and titrated with iron alum soln. Nickel powder can be used in place of Pb in the Jones reductor for the reduction of Fe, Mo, Sn, Ti, U, V and W in 3 to 10 *N* HCl, with or without the aid of heating. Results are no more satisfactory than those with Pb, owing to the colour of $Ni^{\cdot\cdot}$.

K. SAITO

329. **Quantitative chromatography on treated paper. II. Determination of anions.** Akira Murata (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [5], 517–520).—Quantitative chromatographic analysis of 18 anions was studied by the use of paper impregnated with alumina (*cf. Anal. Abstr.*, 1955, **2**, 1443). The widths of the chromatographic bands of OH', PO_4''', F', oxalate, $Fe(CN)_6''''$, SO_3'', SO_4'', CrO_4'', S_2O_3'', $Fe(CN)_6'''$ and IO_3' are independent of the time of developing (with water, 50 min.) and proportional to the amount of the ions within the range 20 to 200 $\times$ 10^{-8} mole. The widths of bands of Cr_2O_7'', acetate, BrO_3', SCN', Cl', Br' and NO_2' increase with increased time of developing; the values are reproducible for a given time of developing, and are proportional to the amounts of the ions. Ions that are adsorbed firmly on the paper give bands that remain unchanged on prolonged developing. The width of bands is practically independent of cations present, but acids give narrower bands than their salts. The specific width of bands (per millimole) is independent of the strength with which ions are adsorbed, but increases with the charge of the ion. K. SAITO

330. **Effect of the distance moved by the solvent on the R_F values in circular chromatography.** D. P. Burma and H. C. Chakrabortty (Bose Res. Inst., Calcutta, India) (*Anal. Chim. Acta*, 1955, **13** [3], 248–252).—The effect of distance (d) travelled by the solvent on the R_F values of amino acids chromatographed by the circular-paper method was determined in an air-tight apparatus, with and without temp. control, for the solvents, phenol saturated with water, and butanol - acetic acid - water (4:1:5). In all instances, the R_F values were approx. independent of d. The different results obtained by Rao *et al.* (*Brit. Abstr. C*, 1953, 1773, 1776) are ascribed to failure to maintain complete saturation inside the cabinet. Butanol - acetic acid - water (4:1:1) at 26° $\pm$ 0·5° C is recommended as an efficient solvent. W. J. BAKER

331. **Ion-exchange chromatography in alcohol.** K. K. Carroll (Univ. of Western Ontario, London, Ontario, Canada) (*Nature*, 1955, **176**, 398–400).—Experiments are described to show that, in ion-exchange chromatography, partition coefficients, based on solubility, between the eluting solvent and the swollen ion-exchange resin affect the order in which compounds are eluted. Results obtained when water or absolute ethanol is used in the eluting solvent in chromatograms with both aromatic and non-aromatic acids are compared. When absolute ethanol is used the technique can be applied to acids and bases with limited solubilities in water, and gives high recoveries.
O. M. WHITTON

332. **Application of ion-exchangers in analytical chemistry. IV. Critical values for quantitative separations and examples for the calculation of working conditions.** D. Jentzsch and I. Pawlik (*Z. anal. Chem.*, 1955, **147** [1], 20–30).—Critical values are given for the quant. separation by Wofatit L 150 of Ca - Zn, Fe - Zn and Al - Fe systems, with approx. wt.-ratios of 1:1 and 1:10. A method of calculation is presented by which the required dimensions of the column can be fixed from numerical data, given in earlier parts, before the beginning of the experiment.
D. R. GLASSON

333. **Zone electrophoresis on filter-paper. A review.** L. F. J. Parker (Glaxo Laboratories Ltd., Greenford, Middlesex, England) (*Analyst*, 1955, **80**, 638–651).—Present knowledge of zone electrophoresis on filter-paper is reviewed and examples of the more elaborate apparatus now in use, as well as the simpler types from which they have been developed, are described, with indications of their applications to particular problems. Some of the theoretical factors controlling the process are considered with practical details, such as choice of filter-paper and buffer solutions. Applications to the separation of proteins, smaller organic molecules, inorganic ions and other uses are described. The future of zone electrophoresis is discussed. (240 references.) A. O. JONES

334. **Indirect spectrophotometry. A study of precision.** J. J. Lothe (Centr. Inst. Ind. Res., Blindern, Oslo, Norway) (*Anal. Chem.*, 1955, **27** [10], 1546–1551).—Indirect spectrophotometry can be used to measure the decolorisation of a solution of a coloured system, and the study of the precision of such methods shows that the lowest relative and lowest absolute errors are obtained at low absorbance readings. The precision can be increased by taking the readings against a partly decolorised standard. A method is given of calculating the error arising from reading the concn. from a calibration curve which, when such a curve flattens out, may be more important than the error that occurs when the concn. is read from the transmittance scale of the instrument. K. A. PROCTOR

335. **Analytical applications of complexones. III. Colorimetric determinations.** F. Bermejo Martínez and A. Prieto Bouzo (Univ. Santiago Compostela, Corunna, Spain) (*Inf. Quím. Anal.*, 1955, **9** [3], 86–94).—Applications of EDTA as a direct reagent for the determination of Ba, Co, Cu, Cr, Fe, Mn, Ni and Pd, and as a sequestering agent in the determination of Al, Be, Bi, Cu, Hg, NO_3', Pd, Ag, Ti, U and V are described. L. A. O'NEILL

336. **Bibliography of publications in 1954 dealing with the polarographic method.** J. Heyrovský (*Coll. Czech. Chem. Commun.*, 1955, **20** [Suppl. 1], 1–61).—A bibliography is given of 946 references to papers on polarography published in 1954, together with 231 references to earlier years that were omitted from previous lists. N. E.

2.—INORGANIC ANALYSIS

337. **The chromatographic examination of metal ions. I.** J. R. A. Anderson and E. C. Martin (N.S.W. Univ. of Technol., Sydney, Australia) (*Anal. Chim. Acta*, 1955, **13** [3], 253–257).—The R_F values of over 40 metal ions have been determined by paper partition chromatography, with butanol saturated with aq. M solutions of various organic acids (citric, malonic, oxalic, thioglycollic, etc.) as solvent, and either (*i*) H_2S or NH_3 or both, or (*ii*) an ethanol solution of 8-hydroxyquinoline and kojic acid with exposure to NH_3 and u.v. light after drying, for development of the spots. The results are listed and discussed in relation to the possible qual. separation of cation mixtures and the quant. separation of cations by selective adsorption or desorption under these conditions.
W. J. BAKER

338. **Applications of chromatography in the analysis of mineral substances. II.** J. Marcé Piera (*Afinidad*, 1955, **32** [147–148], 47–55).—The general

properties of ion-exchange resins are discussed and the uses of the resins and the techniques described in the literature for chromatographic separation of inorganic compounds on them are reviewed. The advantages and disadvantages of the method are discussed. D. LEIGHTON

339. **Paper chromatography of alkali and alkaline-earth cations.** H. T. Gordon and C. A. Hewel (Univ. California, Berkeley, Calif., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1471–1474).—A procedure is described in which Ba^{++}, Sr^{++}, Ca^{++} and Be^{++}, and K^{+}, Na^{+}, Ca^{++} and Mg^{++} are separated by one-dimensional paper-chromatography, *iso*propyl alcohol - pyridine - acetic acid - water being used as developing solvent. The method has particular application to biological fluids. D. A. PANTONY

340. **Micro-determination of alkali metals in silicates.** M. Šimek (Ústav analytické chemie přírodovědecké fakulty, Brno, Czechoslovakia) (*Chem. Listy*, 1954, **48** [10], 1579–1581).—A combination of 8-hydroxyquinoline (**I**) and ammonium oxalate is used for the removal of interfering cations in a single operation. *Procedure*—Evaporate the sample (10 to 20 mg) with 40 per cent. HF (4 ml) and conc. H_2SO_4 (0·2 ml) in a platinum dish, add more HF (1 ml) and again evaporate. Expel H_2SO_4 by heating, wash the contents of the dish into a flask with H_2O (10 ml), add 4 per cent. aq. ammonium oxalate (0·5 ml) and a 4 per cent. soln. of **I** [prepared by dissolving **I** (4 g) in warm glacial acetic acid (8 ml) and diluting with H_2O (88 ml)] (3 to 4 ml), warm the soln. to 60° C, and add dropwise, with constant stirring, 50 per cent. aq. ammonium acetate. Cease the addition when permanent turbidity is obtained; when this changes to a crystalline ppt., add a further quantity (1 ml) of the acetate soln., followed by a dropwise addition of 5 *N* aq. NH_3 until salts of **I** are no longer pptd. Heat the mixture on the steam-bath for 15 min., collect the ppt. after an hour's standing, and wash it with hot H_2O (3 × 0·75 ml) and 1 per cent. aq. NH_3 (3 × 0·75 ml). Evaporate the filtrate to dryness, gently heat the residue to expel ammonium salts, dissolve it in H_2O (2 ml), add H_2SO_4 (1:4) (1 drop), 4 per cent. **I** (1 drop), 4 per cent. ammonium oxalate (0·25 ml), and ppt. the last traces of Ca with aq. NH_3 in the hot soln. Allow the ppt. to stand for 1 to 2 hr., filter and wash it with 0·5 per cent. aq. ammonium oxalate in 1 per cent. aq. NH_3 (3 × 0·75 ml) and with H_2O (2 × 0·5 ml). Evaporate the filtrate, heat the residue, dissolve it in hot H_2O (1 ml), filter the soln. into a weighed platinum crucible, and wash any residue on the filter with H_2O (3 × 0·5 ml). Treat the filtrate with H_2SO_4 (1:4) (1 drop), evaporate, heat the residue for 45 min. at 700° C, and weigh as sulphate. G. GLASER

341. **Indirect colorimetric determination of lithium.** Tôru Nozaki (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [4], 445–448).—Lithium (0·01 to 2 mg) is quant. pptd. on a micro scale with Na_2HPO_4 (in an amount ≃ 6 times the equiv. of the Li) as Li_3PO_4 in the presence of NaOH (≃ 4 times the equiv. of the Li). The P in the ppt. is colorimetrically determined by the molybdenum blue method, in dil. HCl soln. Pure Li_3PO_4 is pptd. even in the presence of K (< 50 times the weight of the Li) and Na (< 67 times). When more K or Na is present, Li is extracted with *iso*butyl alcohol from a conc. soln. of the mixed chlorides. Excess of Na or K can also be removed by adsorption on Amberlite IR–120 and eluting Li with a mixture of methanol (30 per cent.) and 0·2 *N* HCl. K. SAITO

342. **The determination of copper by complexiometric titration with ethylenediaminetetra-acetic acid.** R. Belcher, D. Gibbons and T. S. West (Univ. of Birmingham, England) (*Anal. Chim. Acta*, 1955, **13** [3], 226–229).—A procedure is described for the determination of Cu^{++} by potentiometric titration with EDTA at pH 5 to 6 in the presence of ammonium acetate buffer. The cupric and EDTA solutions should preferably be from 0·1 to 0·5 *N*, and interfering metals (Fe^{III}, Al, Cd, Zn, Mn, Ni, Co and Pb) must be removed by a preliminary separation. W. J. BAKER

343. **The iodimetric determination of copper.** J. Bitskei (Polytechn. Univ., Budapest) (*Magyar Kém. Foly.*, 1955, **61** [1], 23–26).—The author's method (*Brit. Abstr. A*, 1935, 1094) for the iodimetric determination of Cu^{++} is improved. Thiosulphate reduces Cu^{++}; any $[Cu_2(S_2O_3)_2]^{--}$ present are decomposed by SCN^{-} which also combine with and stabilise Cu^{+}. Succinic acid prevents SCN^{-} from using up iodine. *Procedure*—To the measured vol. of Cu^{++} soln. is added 20 per cent. Na K tartrate (10 ml), followed by 20 per cent. KSCN (5 ml). After mixing, 0·1 *N* $Na_2S_2O_3$ (≃ 40 ml or 100 per cent. excess, accurately measured) is added in one portion, very rapidly. After 5 min., the residual $Na_2S_2O_3$ is washed into the soln., which is diluted with water to between 80 and 100 ml. Starch (2 to 3 ml) and 2 per cent. succinic acid (2 ml) are added immediately before the excess of $Na_2S_2O_3$ is titrated with 0·1 *N* iodine solution. A. G. PETO

344. **Coulometric analysis and its application to the quantitative analysis of chromatographic spots. I. Estimation of copper.** Tamotsu Yamada (*Japan Analyst*, 1954, **3** [3], 215–218).—A mercury micro-coulometer of capillary type has been devised and its use for coulometric micro-analysis studied. Metal ions separated by means of chromatography were submitted to electrolysis under a controlled potential and the amounts were determined from the shift of the bubble in the capillary of the coulometer. This apparatus enables the measurement of current equivalent to < 0·03 μg of Cu. A paper-chromatographic spot (R_F = 0·55) of Cu (1 to 100 μg), developed with a mixture of *n*-butanol and 6 *N* HCl (1:1), was extracted with water and electrolysed at − 1·3 V. The current was measured by the coulometer. The average deviation from the mean was < 4 per cent. K. SAITO

345. **Photometric determination of copper in non-ferrous metals and alloys.** H. Pohl (Bundesanstalt Mech. Chem. Materialprüfung, Berlin) (*Metall*, 1955, **9** [3–4], 102–103).—The method described is based on measuring the intensity of the colour of the cuprammonium ion at 630 mμ. The method is applicable to crude and refined Pb and certain non-ferrous metal alloys. By taking the appropriate sample wt., the range 0·002 to 8 per cent. of Cu can be covered. The accuracy is ± 5 per cent. at the 0·002 per cent. of Cu level and ± 0·3 per cent. at the 8 per cent. level. A single determination takes 45 to 60 minutes. C. J. KEATTCH

346. **Reduction of bivalent copper and tervalent iron in a column of ion-exchange resin.** Hidetake Kakihana and Kiyoshi Katou (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [5], 499–503).—The

reduction of Cu^{++} and Fe^{+++}, adsorbed on a cation-exchange resin, was studied with acidic soln. of KI. Cupric ions adsorbed on a column of Amberlite IR–120 (80 to 160 mesh), are quant. reduced by passing KI soln. (0·2 *M*, 100 ml) in 0·1 *M* H_2SO_4 (rate of flow, 1 to 5 ml per min.) to give Cu_2I_2 and I, which can be titrated with $Na_2S_2O_3$. The reduction of Fe^{+++} is much slower than that of Cu^{++}. For the quant. reduction of Fe^{+++} on Amberlite IR–120 (80 to 160 mesh), a more conc. soln. of KI (0·5 *M* in 0·25 to 0·5 *M* H_2SO_4) (200 ml) must be used. The reduction of Fe^{+++} is promoted by treating the column with ether (10 ml) before the passage of the KI soln. K. SAITO

347. **Application of the intermittent-arc method to industrial analysis. I. Determination of a micro amount of copper in fused iron catalysts for ammonia synthesis.** Kumao Ohashi, Eizo Yasui and Hiroshi Suzuki (*J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** [3], 168–170).—The determination of a micro amount of Cu (10^{-2} to 10^{-4} per cent.) in iron catalysts for the synthesis of NH_3 was studied by means of Gillis's extrapolation method (*Anal. Abstr.*, 1954, **1**, 638). The sample is mixed with various amounts of a standard soln. of Cu (14·56 to 0·455 mg of Cu per 100 ml) and the arc spectra are recorded on a photographic plate, together with the spectrum of the sample itself, under the following conditions: 210 V, 4 amp., distance of carbon electrodes 1 mm, ratio of interruption 1:8, period of interruption 1 sec., and exposure 20 sec. The ratio of the intensity of Cu 3273·96 A to that of Fe 3280·6 A is measured on the plate and plotted against the copper contents of the mixed samples. The curve is extrapolated and the copper content of the sample is calculated. The average deviation from the mean is $< \pm 10$ per cent. for 10^{-2} to 10^{-3} per cent. of Cu and $< \pm 20$ per cent. for 10^{-4} per cent. **II. Spectrochemical determination of traces of impurities in common salt, brine and caustic soda.** Eizo Yasui and Hiroshi Suzuki (*Ibid.*, 1955, **58** [3], 170–174).—The simultaneous determination of Si, Fe, Al, Mn and Cu (also, with slight modification, Ca and Mg) in industrial NaCl, brine and NaOH was studied by a similar method. It was found that the application of one drop of a soln. containing 0·5 *M* NaOH and 3·5 *M* NaCl on to the carbon electrode is suitable for quantitative analysis; Cr and Mo are used as internal standards. The sample is dissolved in water and made up to $\simeq$ 200 ml, then a sufficient amount of pure NaOH (for NaCl and brine samples) or HCl (for NaOH) to produce 250 ml of the sample soln. (0·5 *M* NaOH, 3·5 *M* NaCl) is added. Various amounts of the standard soln. containing Si, Fe, Al, Ca, Mg, Cu and Mn are added to this soln. with 0·3 *M* $K_2Cr_2O_7$ and 0·2 *M* $(NH_4)_2MoO_4$ (1 ml each) before making up to a vol. of 250 ml; one sample soln. is prepared without the standard soln. One drop of the sample soln. is placed on the carbon electrode and an intermittent arc is started under the following conditions: 210 V, 4 amp., ratio of interruption 1:3, period 1 sec., preliminary discharge 15 sec. and exposure 90 sec. The ratio of the intensity of the lines to that of the internal standards is plotted against the content of the element concerned in the sample solutions: the diagram is extrapolated to find the initial contents of these elements. For the determination of Ca and Mg, the use of 4 *M* NaCl as the sample soln. is preferred. The conditions for the exposure are modified as follows: for Ca, ratio 1:10, preliminary discharge 30 sec. and exposure 45 sec.; for Mg, 1:8, 5 sec. and 60 sec. The average deviation from the mean is $< \pm 10$ per cent. for Si, Fe, Cu, Mn and Al, 5 to 6 per cent. for Ca, and 2 to 3 per cent. for Mg. K. SAITO

348. **The separation of copper from cadmium by electro-deposition from ammoniacal solution.** H. Diehl and R. Craig (Iowa State Coll., Ames, Iowa, U.S.A.) (*Analyst*, 1955, **80**, 599–601).—Copper can be separated from cadmium by electro-deposition from ammoniacal solution if the cathode potential is limited to −0·73 V *vs.* the S.C.E. and if oxygen is excluded from the electrolyte. The automatic apparatus, electrodes and stirring device have been described previously (Diehl *et al.*, *Brit. Abstr. C*, 1952, 371). Applications of the method to the separation of Cu and Cd and to the determination of Cu and Ag in silver solder are described. A. O. JONES

349. **Concentration of small amounts of copper, antimony and bismuth by co-precipitation.** V. V. Ten'kovtsev (Rostov State Univ., U.S.S.R.) (*Zavod. Lab.*, 1955, **21** [5], 525–527).—To concentrate traces of Cu, Sb and Bi they are introduced into 100 ml of *N* $Pb(NO_3)_2$ and the solution at 100° C is treated with 0·5 g of zinc filings to ppt. the trace metals together with Pb. The solution is continuously stirred, for 5 min. for Sb, 8 min. for Cu and 10 min. for Bi. The ppt. is filtered off by suction on a glass filter, washed with water and dissolved in 2 to 3 ml of hot dil. HNO_3 (1 + 1). Bismuth is determined polarographically in *N* ammonium acetate at pH 5·0 to 6·0, Sb is determined colorimetrically with methyl violet, and Cu is determined volumetrically. G. S. SMITH

350. **Flame-photometric determination of silver in cadmium and zinc sulphide phosphors.** A. O. Rathje (Gen. Elect. Co., Cleveland, Ohio, U.S.A.) (*Anal. Chem.*, 1955, **27** [10], 1583–1585).—In a rapid method for determining $\simeq$ 0·01 per cent. of Ag, the samples are dissolved in HCl and 30 per cent. of acetone is added before measurement of the Ag 338·3-mμ line with an oxy-hydrogen flame. The acetone is added to increase sensitivity, but the addition must be carefully controlled. Interference from Na and Mg can be compensated either by using standards containing these two elements in the same concn. as present in the sample or by measuring the light intensity at 335 mμ and 341 mμ and subtracting the interpolated intensity at 338 mμ. Although small changes in the ratio of Zn to Cd have negligible effect it is advisable to prepare standards with approx. the same concn. of Zn and Cd as found in the sample. For a series of recovery experiments the error ranged from −14·5 to + 11 per cent., being greatest at low concn. of Ag. A practical limit is 5 to 10 p.p.m. of Ag in the phosphors. K. A. PROCTOR

351. **An indirect colorimetric method for the determination of beryllium.** M. Sunderasan and M. Sankar Das (Atomic Energy Estab., 414a Cadell Road, Bombay, India) (*Analyst*, 1955, **80**, 697–699).—The method described is based on the pptn. of $BeNH_4PO_4.6H_2O$, which is subsequently determined spectrophotometrically as molybdophosphoric acid. The soln. of Be is treated with a soln. of $(NH_4)_2HPO_4$, the liquid is made slightly acid to bromocresol green indicator with dil. HCl, and the heated mixture is adjusted to the blue end-point of the indicator (pH 5) with ammonium acetate soln. The liquid is then heated in the water bath

to granulate the ppt., cooled and centrifuged. The ppt. is collected on filter-paper and washed with a soln. of NH_4NO_3 and ammonium acetate (pH 5·3). It is then dissolved in dil. HNO_3, the soln. is evaporated to dryness and the residue is re-dissolved in 2 *N* H_2SO_4; a soln. of Na_2MoO_4 is added, the vol. is adjusted and, after 15 min., the absorption is measured at 390, 400 or 420 mμ. A calibration graph is prepared from standard solutions of Be or of KH_2PO_4. Interference by most elements, including Cu and Ni, is avoided by addition of EDTA before adjusting the pH of pptn. The method is applicable to solutions containing 2 to 20 p.p.m. of Be. A. O. JONES

352. **The spectrographic estimation of submicrogram quantities of beryllium by the cathode-layer technique.** F. T. Birks (Atomic Energy Research Estab., Harwell, England) (*Spectrochim. Acta*, 1955, **7** [4], 231–237).—A Hilger medium quartz or, preferably, a large Littrow quartz spectrograph is used with a 10-amp. d.c. arc. The sample is used as a powdered solid, preferably ≯ 1 mg, or as a soln. evaporated on to shallow-cavity carbon electrodes greased with 1 drop of Apiezon M grease (5 per cent. in light petroleum). Before arcing, 0·1 μg of Mg is added, and the spectra are photographed on Ilford Ordinary plates. By the use of a masking screen only that part of the arc adjacent to the cathode is transmitted and this setting must be reproduced as closely as possible for each exposure. As little as $2{\cdot}0 \times 10^{-11}$ g of Be can be estimated and $1{\cdot}0 \times 10^{-11}$ g detected if the line contour of Be 2348·61 A and of the background structure is traced and recorded by a microphotometer. Iron interferes if present in large amount, but 5×10^{-11} g of Be can be detected in the presence of 50 μg of Fe. No Be has been detected in high-purity graphite from three different sources. K. A. PROCTOR

353. **Rapid method for determination of magnesium in nodular cast iron using EDTA.** H. Green (Alvechurch, Birmingham, England) (*J. Brit. Cast Iron Res. Ass.*, 1955, **6** [1], 20–22).—A method for determining Mg in nodular cast iron, which can be carried out in 2 hr., consists in titration with EDTA (disodium salt), after separation from other elements. *Procedure*—To 10 g of sample dissolved in 80 ml of HNO_3 (1 + 1) in a 600-ml beaker add 40 ml of $HClO_4$ (sp. gr. 1·54) and evaporate to fuming. Fume for 2 to 3 min., cool slightly and dilute with 300 ml of boiling H_2O; stir till dissolved and add 25 g of ZnO, stir and add 2 g of $(NH_4)_2S_2O_8$. Boil for 10 min. to ppt. Fe, Mn, etc. Add 5 ml of ethanol, boil the soln. for 5 min., cool and place in a 500-ml flask. Transfer 250 ml of the filtrate to a 600-ml beaker and add 4 to 6 g of NH_4Cl. Add NaCN solution (250 g per litre) till the ppt. formed redissolves, then add a further 10 ml. Add 10 ml of aq. NH_3 soln. and 5 ml of 0·5 per cent. Tiron (catechol-3:5-disulphonic acid); allow the soln. to stand for 2 min. Into this soln. run 10 ml of EDTA (1 per cent.) with a semi-micro burette, and titrate with standard magnesium soln. in the usual way. Since group 3 metals are not reprecipitated the method is not stoicheiometric, and a factor must be determined from the recovery of known amounts of Mg. C. H. COWPER-COLES

354. **Determination of oxygen in calcium metal.** A. R. Eberle, M. W. Lerner and G. J. Petretic (U.S. Atomic Energy Res. Comm., New Brunswick, N.J., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1431–1433).—The sample is treated first with methanol, then with a mixture of salicylic acid and pyridine. Water is liberated stoicheiometrically from the calcium oxide present, and is determined by the Karl Fischer method. The water is directly related to the oxygen content. D. A. PANTONY

355. **Precipitation of barium carbonate.** H. Teicher (Monsanto Chemical Co., Miamisburg, Ohio, U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1416–1418).—Barium carbonate is precipitated almost quantitatively by passing CO_2 into an ammoniacal soln. of Ba^{++}. After addition of ethanol (20 per cent. v/v), the dense ppt. is easily filtered off and is then washed with 90 per cent. v/v aq. ethanol. D. A. PANTONY

356. **Morphology of barium sulphate as seen through electron microscopy.** S. Okada and S. Magari (Kyoto Univ., Kyoto, Japan) (*Anal. Chem.*, 1955, **27** [9], 1481–1484).—Morphological data for $BaSO_4$ pptd. under various conditions and examined by the electron microscope are presented. D. A. PANTONY

357. **Zinc mercurithiocyanate method and its application to yellow-metal alloys.** C. L. Rulfs and L. J. Kirby (Univ. Michigan, Ann Arbor, Mich., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1498–1499).—Zinc in brass is determined by pptn. as zinc mercurithiocyanate after removal of lead and copper by standard procedures. D. A. PANTONY

358. **Aromatic hydroxy acids as reagents in inorganic analysis. III. Coumaric acid as a specific reagent for mercurous ions.** A. Waksmundzki and B. Szucki (Medical Academy, Lublin, Poland) (*Ann. Univ. M. Curie-Skłodowska*, **AA**, 1953, **8** [3], 17–34).—Coumaric acid in 50 per cent. alcoholic solution is shown to be a quant. reagent for Hg^{I} in the presence of a large excess of Hg^{II}; Ag^{+} interfere when the free acid, and Hg^{II}, Ag^{+} and Pb^{++} when the ammonium salt, is used. The Hg^{I} is pptd. as $HgC_9H_9O_3.HgNO_3$ from soln. containing NO_3', and the gravimetric and conductimetric procedures are given. A concn. of 14 μg of Hg^{I} per ml can be detected, and the accuracy is ± 2 per cent. in the presence of a great excess of Hg^{II}, improving with lower concn. of Hg^{II}. S.C.I. ABSTR.

359. **Spectrographic determination of trace quantities of boron in steel.** E. F. Runge, L. S. Brooks and F. R. Bryan (Ford Motor Co., Dearborn, Mich., U.S.A.) (*Anal. Chem.*, 1955, **27** [10], 1543–1546).—A quantitative spectrographic procedure for the determination of B in steel in the range 0·0001 to 0·0006 per cent. is described. The method involves measurement of the B 2497·73-A line resolved from Fe 2497·82 A by the use of a Bausch and Lomb echelle attachment combined with a Littrow quartz-prism spectrograph (Kirchgessner and Findelstein, *Brit. Abstr. C*, 1953, 460). The sample, in the form of a slug, is arced in a preformed graphite anode. Only the initial portion of the arcing period is recorded in order to improve line-to-background ratio, sufficient spectral intensity being obtained by superimposing several spectra. The precision is ± 10 per cent. at a concn. of B of 0·0003 per cent., and accuracy is estimated to be within 0·00005 per cent. of B. K. A. PROCTOR

360. **Preparation of spectrographic standards of low boron content for determination of boron in iron.** J. C. Shyne and E. R. Morgan (Ford Motor Co., Dearborn, Mich., U.S.A.) (*Anal. Chem.*, 1955, **27**

[10], 1542–1543).—Precise standards for the spectrographic determination of B in steel containing as little as 1 p.p.m. of B can be made by using vacuum melting techniques and careful ingot processing. K. A. PROCTOR

361. **Determination of traces of boron in graphite, uranium, and beryllium oxide.** J. Coursier, J. Hure and R. Platzer (*Rapp. Centre Et. Nucl. Saclay*, 1955, No. 404, 11 pp.).—The method described is based on the colorimetric reaction of borates with curcumin (**I**). *Procedure*—To 25 ml of test solution is added 1 ml of a 0·125 per cent. alcoholic solution of **I**. Extinction measurements, with light of wavelength 540 mμ, are carried out on a series of solutions to which various known amounts of B have been added, and on the corresponding blanks. Detailed methods are described for the extraction of BeO, U and graphite to prepare the appropriate test solutions. As little as 0·05 p.p.m. of B can be determined by this method. S.C.I. ABSTR.

362. **Colorimetric determination of borate as poly(vinyl alcohol) - borate - iodine complex.** R. F. Muraca and E. S. Jacobs (Lehigh Univ., Bethlehem, Pa., U.S.A.) (*Chemist Analyst*, 1955, **44** [1], 14–16).—The formation of a blue colour when ferric sulphate and iodine soln. are added to an acid soln. containing poly(vinyl alcohol) and borate has been used for the quant. colorimetric determination of borate. For a 3-ml sample, concn. of B $>$ 300 p.p.m. give a blue coloration immediately, but 80 p.p.m. can be detected if the mixture is set aside for about 30 minutes. Most ions that interfere can be removed by oxidation or pptn. as sulphides.
O. M. WHITTON

363. **Determination of aluminium in plain steel using EDTA and dichlorodiethyl ether.** C. Elliott and J. W. Robinson (P.O. Eng. Dept., Birmingham, England) (*Anal. Chim. Acta*, 1955, **13** [3], 235–238).—In the gravimetric procedure described, most of the Fe is first removed by shaking a solution of the sample (in conc. HCl) with steam-distilled dichlorodiethyl ether, followed by separation of interfering metals by pptn. with aq. NH_3 and NH_4Cl, redissolution in HCl, and then complexing with EDTA (disodium salt). The resulting solution is adjusted to pH 11 with KOH and boiled, and the ppt. (Mn and Fe) is filtered off. The filtrate is neutralised, then concentrated to $\simeq$ 20 ml, and Al is pptd. with oxine at 60° C in the usual way.
W. J. BAKER

364. **Flame-spectrochemical analysis. I. Determination of a micro amount of sodium in aluminium metal.** Shigerô Ikeda (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [4], 354–357).—The spectrophotometric determination of sodium (0·001 to 0·01 per cent.) in aluminium metal of high purity can be effected by the use of a Beckman DU photometer (model 9200). The sample (1·5 g) is dissolved in HCl (1 + 1) (30 ml) and made up to 100 ml. An oxy-hydrogen flame is used (pressure of H, 1·5 lb per sq. in.; pressure of O, 25 lb) and the intensity of the spectral line is measured at 589 mμ. The standard soln. is prepared from NaCl and aluminium metal free from Na. The intensity of the background must be subtracted. No interference results from the presence of Ca ($<$ 30 μg per ml), Cu ($<$ 60 μg), Fe ($<$ 50 μg), Mg ($<$ 100 μg) and K ($<$ 3 μg). The average deviation from the mean is $\pm$ 9 per cent. for 0·001 per cent. of Na in Al. K. SAITO

365. **The paper-chromatographic separation of quadrivalent germanium. The evaluation of the chromatogram.** Z. Nagy and E. N. Pólyik (*Magyar Kém. Foly.*, 1955, **61** [8], 248–249).—Chloroform extracts Ge^{IV} from an HCl soln. and thus Ge^{IV} can be separated from the other metals by using $CHCl_3$ - ethanol - conc. HCl (17 : 7 : 1, by vol.) in the ascending method. After being dried at 60° to 70° C, the paper is sprayed with morin (0·3 per cent. in ethanol). On strips of Macherey Nagel 214 paper, 12 cm wide, the R_F is 0·60, measured from the brown strip behind the solvent front. This differs considerably from other metals that react with morin. The sensitivity is 0·1 μg of Ge^{IV}. By comparing the size and intensity of the spot with simultaneously applied known samples, the concn. can be estimated.
A. G. PETO

366. **The spectrographic determination of the germanium content of coal.** G. Szádeczky-Kardoss and I. Benkö (*Magyar Kém. Foly.*, 1955, **61** [8], 225–234).—The method is suitable for the determination of Ge (0·01 to 0·001 per cent.) in coal-ash, without enrichment. The coal is ashed with access to air, at 400° C, and the sample (30 mg), dried at 120° C, is placed in the carbon anode (diameter 5 mm); diameter of hole 4 mm, depth 3 mm; slit-width, 0·025 mm; time of exposure, 9 sec. Under these conditions, GeO_2, GeS_2 or $MgGeO_4$, mixed into coal-ash or oxides, gave the same ratio for the intensities of the Ge and Sn lines, with $\gtrsim$ 6 per cent. error. The standard samples are prepared from Ge-free ash or oxide and GeO_2. The evaluation is carried out with the main calibration curve, without comparative samples, using the ratio of the intensities of the Ge 3039 to Sn 3032 lines. Above 0·004 per cent. of Ge, no correction for interfering radiation is needed; in the 0·004 to 0·0004 per cent. region, the Ge 3039 line is corrected for Fe 3039·3 plus the fundamental radiation, the Sn 3032 line is corrected for the fundamental radiation. The correction of the interfering 3039·3 line is based on that of the Fe 3014 line. The reproducibility, expressed as mean relative error, is $\pm$ 3 per cent. when the content of Ge is $>$ 0·001 per cent. The max. systematic error is $\simeq$ 6 per cent. The results agree well with those from the photometric phenylfluorone method. A. G. PETO

367. **The spectrographic determination of germanium in coal and flue dust.** G. J. Pitt and the late M. F. Fletcher (National Coal Board, Stoke Orchard, nr. Cheltenham, England) (*Spectrochim. Acta*, 1955, **7** [4], 214–218).—The sample is ashed at $\gtrsim$ 400° C, the ash is mixed with four times its wt. of Li_2CO_3 (containing 0·1 per cent. of Sn) and this mixture is made into pellets of about 10 mg, which are placed in a cavity electrode (anode) and burnt to completion in a d.c. arc at 9 amp. A large dispersion quartz-prism spectrograph is used and the spectra are photographed on Ilford Ordinary plates, developed for 4 min. in I.D.2 at 67° F $\pm$ 0·5° F. The Seidel density differences of Ge 2651·18 A and Sn 2546·55 A are measured, and the concn. of Ge is obtained from a calibration graph prepared by arcing standard mixtures containing from 3 to 200 p.p.m. of Ge in the Li_2CO_3 flux. When the content of Ge is $<$ 30 p.p.m., a background correction is applied on the assumption that Seidel densities are additive, and in this way a linear calibration graph over the range 6 to 200 p.p.m. of Ge is obtained. If the sample contains $>$ 7 per cent. of Fe, a correction must be applied to the tin line because of the adjoining iron line at 2545·98 A.

The lower limit of detection is 6 p.p.m. on the ashed sample, but for quant. estimation the useful range is from 24 p.p.m. upwards, when the coeff. of variation is 5 per cent. between exposures on one plate. Agreement between this method and a colorimetric method (Cluley, *Analyst*, 1951, **76**, 523) is reasonably good. K. A. PROCTOR

368. **Use of morin in chemical analysis. III. Photometric determination of quadrivalent tin.** V. Patrovský (Ústřední ústav geol., Prague, Czechoslovakia) (*Chem. Listy*, 1954, **48** [11], 1694–1695).—A colorimetric method for the determination of Sn^{IV}, based on the formation of a blue complex of Sn^{IV} with morin in a weakly acidic soln., is described. *Procedure*—The sample (0·1 to 0·3 g) is dissolved in the min. quantity of HNO_3, 0·5 ml of conc. HCl is added and the soln. is evaporated almost to dryness; the residue is moistened with conc. HCl and again evaporated. The residue is dissolved in 2 ml of conc. HCl, the soln. is diluted with 10 ml of H_2O, cooled, treated with 2 ml of a 0·2 per cent. soln. of morin in 50 per cent. ethanol, diluted to 50 ml and the extinction is measured, a violet filter of max. transmittance at 430 mμ being used. The procedure is applicable even in the presence of a considerable excess of Cu, but Sb, Ti, Mo, W, Ta, Nb, Zr, Th, F′, oxalates and excess of tartrates interfere. G. GLASER

369. **Polarographic determination of tin and antimony in iron and steel.** Hidehiro Gotô, Shigerô Ikeda and Shiro Watanabe (*Japan Analyst*, 1954, **3** [4], 320–323).—Both Sn (0·5 to 5 mg) and Sb (0·2 to 2 mg) are co-precipitated with MnO_2 and separated from most of the Fe and other components of steel. The Sn is reduced to $Sn^{\cdot\cdot}$ with aluminium foil in dil. HCl and determined by polarography ($E_{\frac{1}{2}} = -0{\cdot}47$ V *vs.* the S.C.E.) in a soln. containing HCl, NH_4Cl and $MnCl_2$; Sb is determined by polarography ($E_{\frac{1}{2}} = -0{\cdot}23$ V) in a soln. containing H_2SO_4, HCl and $MnCl_2$. Neither Sn nor As (< 5 mg) interferes with the result for Sb. A small amount of Fe, which is inevitably contained in the MnO_2, can be reduced with hydrazine sulphate to $Fe^{\cdot\cdot}$, which does not affect the polarogram of Sb. *Procedure*—The sample (5 g) is dissolved in HNO_3 (1 + 1) (120 ml) and diluted with water (150 ml) and $MnSO_4$ soln. (20 per cent.) (10 ml). The soln. is treated with small portions of *N* $KMnO_4$ (5 ml) and heated to boiling point. The ppt. is filtered off and washed with water. For the determination of Sn the ppt. is dissolved in 3 *N* HCl (20 ml) and a small amount of H_2O_2 and boiled to decompose the excess of H_2O_2. The soln. is heated in a current of CO_2 with NH_4Cl (10 g) and aluminium foil (0·2 g) until the Al is dissolved. The product is cooled, made up to 50 ml (including 2 ml of 0·2 per cent. gelatin soln.) and submitted to polarography. For the determination of Sb, the ppt. of MnO_2 (see above) is dissolved in 6 *N* H_2SO_4 (10 to 15 ml) and a small amount of H_2O_2 and heated gently until white fumes are evolved. The product is cooled, dissolved in 6 *N* H_2SO_4 (5 ml), treated with hydrazine sulphate (1 g) to reduce $Fe^{\cdot\cdot\cdot}$ to $Fe^{\cdot\cdot}$, and made up to 25 ml after adding 1 ml of 0·2 per cent. gelatin soln. The soln. is submitted to polarography. K. SAITO

370. **Spectrographic analysis of nominally pure lead.** Brit. Non-Ferrous Metals Res. Ass., Spectrographic Research Committee, Lead Analysis Panel (*Spectrochim. Acta*, 1955, **7** [4], 205–213).—This report summarises the results of co-operative investigations by six laboratories into the spectrographic determination of trace impurities in Pb. Of the four methods of excitation employed, *viz*, B.N.F. general-purpose source unit, high-capacity condensed spark, high-voltage spark with Levy trigger, and condensed spark, no one method is recommended as superior, and different elements require different optimum conditions. Methods have been developed for the determination of Ni, Bi, Tl, Cd, Sb, Ag, Sn, Cu, Zn and Te in the range 0·0005 to 0·005 per cent. For all these elements one or more of the methods used gives a reproducibility of ± 10 per cent. at the higher concn., but the accuracy of all the methods deteriorates with decreasing concn. The sensitivity and accuracy of the methods recommended are better than of those in current use. The preparation of a range of standard alloys is described in an appendix.
K. A. PROCTOR

371. **Inorganic circular-paper chromatography: separation of lead, mercury, bismuth, copper and cadmium ions.** A. R. Vasudeva Murthy and V. A. Narayan (Indian Inst. Sci., Bangalore) (*Naturwissenschaften*, 1955, **42** [15], 439).—Pollard *et al.* (*Brit. Abstr. C*, 1951, 317) observed a slight difference in the R_F values of the anions when different copper salts were chromatographed with butanol - acetic acid as solvent. Modification of experimental conditions has enabled different salts of the same cation to be separated. Solutions (0·1 *M*) of the different salts of Pb, Hg, Bi, Cu and Cd were spotted separately at the centre of a filter-paper (Whatman No. 3) and chromatographed with different solvents. Mixtures of the sulphate, chloride and nitrate as well as sulphate, chloride and acetate of copper and cadmium were also chromatographed, *n*-butanol saturated with 4 *N* acetic acid being used as solvent. The metals separated in three concentric rings, corresponding to sulphate, chloride and nitrate in one case, and sulphate, chloride and acetate in the other. These results indicate the marked influence of the nature of the acid used with the irrigating solvent on the R_F values of cations.
S. R. NEUBERGER

372. **Analytical chemistry of titanium alloys.** M. Codell, G. Norwitz and J. J. Mikula (Pitman-Dunn Lab., Frankford Arsenal, Philadelphia, Pa., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1379–1383).—Sampling, dissolution and the analytical chemistry of titanium alloys are reviewed. The formation of soluble titanium complexes, separations of constituents, use of instrumental methods and the determination of Al, B, Ca, C, Cl, Cr, Co, Cu, H, Fe, Mg, Mn, Mo, Ni, Nb, N, O, P, Si, Ag, S, Ta, Sn, Ti, W, V and Zr are discussed. (68 references.)
D. A. PANTONY

373. **Spectrophotometric determination of traces of titanium in uranyl nitrate.** R. Fernández Cellini and T. Batuecas Rodríguez (*An. Real Soc. Esp. Fis. Quím.*, 1955, **51**B [6], 409–416).—The Ti is determined spectrophotometrically as the Ti-thymol complex after pptn. of the U as peroxide at controlled pH. The absorption max. is at 440 mμ and Beer's law is obeyed over a wide range of concn. The preferred working concn. is 5 to 60 μg of Ti in 10 ml. The sensitivity is about 10 times that of the H_2O_2 method. Concentrations of W and V $\not>$ 1000 μg in 10 ml do not interfere. *Procedure*—Uranyl nitrate (≃ 1 g) is dissolved in 50 ml of H_2O, warmed to 60° C and 0·8 ml of H_2O_2 (30 per cent.) is added drop by drop, $UO_4.2H_2O$ being pptd. The pH falls to between 1 and 1·4

and is brought back to 2·5 by gradual addition of 0·1 *N* aq. NH_3. After 3 hr. the ppt. is filtered off and washed with 1 per cent. H_2O_2 acidified with HNO_3 to between pH 2 and 2·5. The filtrate is treated with 5 ml of conc. H_2SO_4, evaporated until fumes of SO_3 appear, and cooled; 0·3 ml of thymol reagent (1 per cent. in conc. H_2SO_4) is added, the vol. is made up to 10 ml with conc. H_2SO_4 and the absorption is measured at 440 mμ. The reagent is best prepared by dissolving the thymol in a little glacial acetic acid and ethanol (10:1) and slowly adding this soln. to conc. H_2SO_4 cooled in a freezing mixture in the dark. L. A. O'NEILL

374. **Differential spectrophotometric determination of zirconium.** D. L. Manning and J. C. White (Oak Ridge National Lab., Oak Ridge, Tenn., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1389–1392).—Zirconium is determined spectrophotometrically by a differential technique by measuring the absorption, at 530 mμ, of the colour produced with alizarin red S in *M* $HClO_4$ soln. The method is rapid and its precision compares well with that of the gravimetric mandelic acid method. D. A. PANTONY

375. **The determination of zirconium in its binary alloys with niobium and tantalum.** G. W. C. Milner and J. W. Edwards (Atomic Energy Res. Estab., Harwell, England) (*Anal. Chim. Acta*, 1955, **13** [3], 230–234).—In the procedure, described in full, most of the Nb or Ta is removed by extraction with *iso*butyl methyl ketone from a soln. (in HNO_3 and HF) that has been equilibrated with 10 *M* HF and 6 *M* H_2SO_4; the soln. of the sample should contain from 5 to 100 mg of Zr. The Zr is then separated from unextracted Nb or Ta by a double pptn. (in a centrifuge tube) with aq. NH_3 in the presence of H_2O_2 to sequester Nb or Ta and ensure complete pptn. of $Zr(OH)_4$. The washed ppt. is dissolved in HCl (1 + 1), an excess of standard EDTA soln. is added (with adjustment of pH to between 5 and 6) and, after the soln. has been boiled for 2 min. and cooled to room temp., the excess of EDTA is titrated with standard iron soln. Recovery of Zr is 99·5 to 100 per cent.
W. J. BAKER

376. **Spectrochemical analysis of zirconium in silicate rocks (with special reference to the spectroscopic buffer for zirconium).** Hiroshi Hamaguchi and Rokuro Kuroda (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [5], 524–527).—In order to increase the sensitivity of the arc spectral lines of Zr, a number of salts were tested for use as the spectroscopic buffer. It was found that the addition of $BaCl_2$ or AgCl decreases the differential evaporation and increases the sensitivity of the detection. The sample is mixed with an equal weight of $BaCl_2$ and put into a small hole in a carbon electrode. An arc (170 V, 7 amp.) is struck and, after 40 sec., exposure is given for 50 sec. The detection of ≮ 0·0002 per cent. of Zr in silicate rocks can be effected by the use of the lines Zr 3428·23 A and Zr 3391·98 A. K. SAITO

377. **Diphenic acid as an analytical reagent for thorium.** G. Banerjee (*Naturwissenschaften*, 1955, **42** [14], 417).—Diphenic acid (diphenyl-2:2′-dicarboxylic acid) can be used for the gravimetric determination of small amounts of Th. The reagent can be prepared from diazotised anthranilic acid by treatment with a cuprammonium - sulphite reducing agent. Thorium forms a voluminous ppt. with the reagent which settles quickly even without the presence of NH_4NO_3 as electrolyte. The ppt. is quant., stoicheiometric in composition and insol. in H_2O, and can be directly weighed as $Th(C_{14}H_8O_4)_2$ when Th is being determined in pure soln. and in the presence of added co-solutes. Thorium can be pptd. from hot soln., neutralised to Congo red, by the free acid alone, although the presence of a little ammonium acetate brings down the ppt. even in the cold. Since Th is not pptd. in the acid medium, but Zr is, the Zr can be pptd. below pH 2; the co-determination of these elements is thus possible. Only a few metals, *e.g.*, Fe^{III}, Ce^{III}, Hg^{I} and Ag, interfere. The interference of $Fe^{\cdots}$ can be avoided by adding ascorbic acid and Th can then be pptd. by the ammonium salt of the reagent. S. NEUBERGER

378. **Determination of thorium by organic bases.** G. S. Deshmukh and J. Xavier (*Bull. Chem. Soc. Japan*, 1955, **28** [4], 233–234).—A method is described for the determination of Th and its separation from Ce, La, Yb and Er in aq. soln., by pptn. with *o*-anisidine or *o*-phenetidine. To 10 ml of a soln. containing Th (chloride or nitrate) are added 20 to 30 ml of ethanol, and the soln. is heated to 90° C; a saturated soln. of the base in alcohol is added with stirring, until pptn. is complete, after which 5 to 10 ml of ethanol are added and the soln. is boiled again for 2 min. The settled ppt. is filtered off, washed with cold ethanol, ignited and weighed as ThO_2. G. R. WHALLEY

379. **A spectrographic procedure for the quantitative determination of trace elements in galena.** F. Hegemann and C. von Sybel (Mineralog.-Geolog. Institut, Techn. Hochsch., Munich) (*Metall*, 1955, **9** [3–4], 91–96).—The sample is introduced into a hollow electrode and excited by an 8-amp.-triggered arc. The sample is made positive for the determination of moderately and easily volatile elements. In order to obtain a greater sensitivity with easily volatile elements, such as As and Zn, the sample is arced for a second time as the cathode for up to 30 sec. Thallium is determined by a separate method, in which the CN′ bands are suppressed with KCl. The intensities of the lines are recorded on the spectrogram and are measured photometrically or visually with the s.p.d. procedure. Gallium is used as the "group reference element" for moderately volatile elements, and Cd for those that are not readily volatile. C. J. KEATTCH

380. **Spectrophotometric determination of phosphorus as molybdovanadophosphoric acid.** K. P. Quinlan and M. A. DeSesa (Nat. Lead Co., Inc., Winchester, Mass., U.S.A.) (*Anal. Chem.*, 1955, **27** [10], 1626–1629).—An extensive survey of the molybdovanadophosphoric acid method (Misson, *Chem.-Ztg*, 1908, **32**, 633) for the determination of P has been made. The optimum colour development was found in solutions which are 0·4 *M* in acid, 0·02 to 0·06 *M* molybdenum^{VI} and 1·0 to 4·0 m*M* vanadium^{V}. The optimum range is 3 to 20 p.p.m. of P_2O_5 for 1-cm cuvettes, measured at 400 mμ. The only serious interference is from $Cr_2O_7^{\prime\prime}$, which can be eliminated by volatilisation of the Cr as chromyl chloride. K. A. PROCTOR

381. **Estimation of arsenic by paper chromatography.** I. I. M. Elbeih (Univ. Cairo, Giza, Egypt) (*Chemist Analyst*, 1955, **44** [1], 20–21).—By the method described, 0·3 μg of As in 0·01 ml of sample solution can be detected. A saturated butanol - water solution containing ammonium tartrate,

ammonium borate and mannitol is used for the separation, and the paper chromatogram is sprayed with alcohol containing 1 per cent. of HNO_3 and 5 per cent. of glycerol and, after being dried, with ammoniacal $AgNO_3$ solution. The spot of As is converted into yellow Ag_3AsO_3 which, on irradiation with u.v. light while still wet, is changed to brown Ag_3AsO_4 and black metallic As. Excess of acidity prevents identification. The concentration of As in the sample is estimated by comparing the intensity of the colour of the spot with the colours formed by standard solutions. Antimony, tin and mercury do not interfere. O. M. WHITTON

382. **The concentration of arsenic from silicate rocks for a colorimetric or spectrographic determination. Decomposition by hydrofluoric acid under pressure.** K. Lounamaa (Bolidens Gruvaktiebolag, Skelleftehamn, Sweden) (*Z. anal. Chem.*, 1955, **146** [6], 422–429).—Processes for the separation and concentration of As from silicate rocks are followed by the colorimetric molybdenum blue and by spectrographic analytical methods. The finely powdered (< 100 mesh) test samples (1 g) are heated with $HClO_4$ (4 ml) for 5 to 10 min., then completely decomposed by being heated with conc. HF (15 ml), NH_4HSO_3 (2 ml) and NH_4I (0·1-g crystal) in a Teflon-lined steel bomb for 1 hr. at 150° C. Any remaining insol. contents are then centrifuged and washed with dil. HF (1:10). The As is isolated from the filtrate by pptn. with diethyldithiocarbamate (15 ml) and extraction with $CHCl_3$. Under these conditions only Cu and part of the Bi are extracted with the As. Organic substances are removed by further treatment with mixed acid (4 ml of equal vol. of conc. H_2SO_4, HNO_3 and $HClO_4$) or with $Mg(NO_3)_2$. After being neutralised with conc. aq. NH_3, the solution is mixed with molybdate reagent and reduced by hydrazine, the absorption being measured at 840 mμ. In the spectrographic determination, Te (40 μg) is added as a reference element. The methods permit determination of 0·0005 to > 0·05 per cent. of As in silicate rocks to an accuracy of ± 10 per cent. D. R. GLASSON

383. **Modification of a method for the rapid electro-analytical separation of antimony and tin.** M. S. Jovanović (Chem. Tech. Inst., Belgrade) (*Bull. Soc. Chim., Belgrade*, 1955, **20**, 39–45).—Both metals are dissolved by heating in 10 ml of conc. H_2SO_4; a further 40 ml of acid are added and water to about 150 ml. The antimony is then electrolysed at a terminal voltage of 2 to 2·1 V until the current strength falls to between 0·1 and 0·2 amp. The separation is now complete, but the electrolysis is continued for a further half hour; the deposit now adheres strongly to the cathode. The remaining solution can be used for the determination of tin by the method of Sand (*J. Chem. Soc.*, 1908, **93**, 1583) or with bromate after reduction with nickel. N. E.

384. **Spectrophotometric determination of quinquevalent vanadium with benzohydroxamic acid and *n*-hexanol. Application to steels and crude and residual oils.** W. M. Wise and W. W. Brandt (Purdue Univ., W. Lafayette, Ind., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1392–1395).—Small amounts of V are determined by conversion into the benzohydroxamic acid salt at pH 2, and extraction with *n*-hexanol. The absorption of the extract is measured at 450 mμ. Strong oxidising and reducing reagents interfere. The method is applied to the determination of V in steel and oil, from which excesses of Fe^{+++} are removed by electrolysis with a mercury cathode before colour development. D. A. PANTONY

385. **Colorimetric determination of niobium in the presence of titanium.** R. J. Mundy (National Lead Co., Sayreville, N.J., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1408–1412).—After an examination of the spectral properties of the thiocyanate complexes of Ti and Nb and certain other cations, a procedure based on the measurement of absorption of the complexes at 360 mμ and 400 mμ is recommended. The concentration - absorption relationships are not linear, and concn. are derived from calibration curves. D. A. PANTONY

386. **The quantitative separation and determination of tantalum and niobium using anion-exchange chromatography.** M. J. Cabell and I. Milner (Atomic Energy Res. Estab., Harwell, England) (*Anal. Chim. Acta*, 1955, **13** [3], 258–267).—The almost complete chromatographic separation of > 100 mg each of Nb and Ta in a soln. equilibrated with 3 *M* HCl - 0·1 *M* HF, and the quant. determination of the elements thus separated are described in full. Separation is effected by passing the soln. through a column (12 cm × 1·3 sq. cm) of De-Acidite FF (− 120 to + 200 B.S. sieve) in polythene tubing to retain both elements. Niobium is then rapidly eluted with 3 *M* HCl - 0·1 *M* HF as eluent (flow rate ≃ 10 ml per min.), the first fraction of the eluate (≃ 30 ml) being rejected, whilst the Ta is finally recovered by elution with 4 *M* NH_4Cl - *M* NH_4F at a flow rate of ≃ 2·5 ml per min. The two metals are then determined gravimetrically as Nb_2O_5 and Ta_2O_5 by a double pptn., first with aq. NH_3 and then with tannic acid, in each eluate. Recovery of each metal is from 99 to 99·5 per cent., and there is < 0·01 per cent. of Ta in the Nb fraction. A modified separation procedure permits production of gram amounts of Nb containing > 5 p.p.m. of Ta. Iron, Ti and W will contaminate the Nb fraction, and Sn the Ta fraction. W. J. BAKER

387. **Spectrophotometric determination of tantalum.** B. Sarma and J. Gupta (*J. Indian Chem. Soc.*, 1955, **32** [5], 285–290).—A spectrophotometric method for the estimation of 10 to 200 p.p.m. of Ta in an oxalic acid - HCl - H_2SO_4 mixture (0·2 to 2 *N*) is described; the complexing agent is catechol. The Ta - catechol complex is yellow in acid media, with an absorption max. at 395 mμ. The presence of Ti causes interference which can be minimised by working at an acidity of 1·5 to 2 *N*. Phosphate, fluoride and tartrate also interfere. Niobium does not interfere over a wide range of acidity, nor does oxalate, sulphate or chloride. A. JOBLING

388. **Volumetric method of determining sulphur in pyrites and combustion residues.** V. Glabisz (*Przem. Chem.*, 1954, **10**, 493).—A volumetric method, quicker than gravimetric (1½ hr.) but equally accurate (± 0·25 per cent.), has been developed. It involves oxidation of the pyrites or combustion residues to sulphate, removal of Fe as hydroxide, and pptn. of the SO_4'' with $BaCl_2$. The ppt. is dissolved in oxalate - acetate - chromate mixture, then made up to standard volume, and portions are treated with KI and HCl soln., the liberated I being titrated with $Na_2S_2O_3$ soln. A. O. JAKUBOVIC

389. **Rapid micro-titration of sulphate.** J. S. Fritz and S. S. Yamamura (Iowa State College, Ames, Iowa, U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1461–1464).—The soln. is passed through a cation-exchange column and the SO_4'' in the eluate is determined by titration with $Ba(ClO_4)_2$ in 80 per cent. aq. ethanol, thorin being used as indicator.
D. A. PANTONY

390. **Semi-micro determination of sulphates.** P. Blanc, P. Bertrand and L. Liandier (*Chim. Anal.*, 1955, **37** [9], 305–307).—The nephelometric determination of SO_4'' in waters, wines and biological liquids can be effected by pptn. of $BaSO_4$, in slightly acid (HCl) soln., with 10 per cent. aq. $BaCl_2$ containing 20 per cent. of a strongly dispersive surface-active agent, *e.g.*, polyoxyethylenesorbitol monolaurate (Tween 20). The opacity of the suspension is measured, after 15 min., in an electrophotometer having a blue filter. The sample (40 ml, or diluted to 40 ml) should not contain > 50 mg of SO_4'' per litre. The results agree well with those obtained gravimetrically.
W. J. BAKER

391. **Determination of low concentrations of sulphate using barium chloride and ethylenediaminetetra-acetic acid (EDTA).** R. D. Bond (Division of Soils, C.S.I.R.O., Australia) (*Chem. & Ind.*, 1955, [30], 941–942).—Four titrations are required. (i) To determine Ca and Mg, a suitable aliquot is diluted to 50 ml, then a mixture (**I**) of 5 ml of *N* NH_4Cl, 3 ml of conc. aq. NH_3 and a few drops of Eriochrome black T are added before titrating with 0·01 *N* EDTA. (ii) A $BaCl_2$ soln. is standardised by mixing 10 ml with 2 ml of 0·01 *N* $MgCl_2$ and **I**, diluting to 50 ml, and titrating with EDTA. The vol. equiv. to the titration blank and the added $MgCl_2$ is deducted. (iii) To determine SO_4'', HCl is added to an aliquot of the sample, $\geqslant$ 50 ml, containing $\geqslant$ 0·05 milli-equiv. of SO_4'' per litre and $\geqslant$ 0·15 milli-equiv. of Ca and Mg per litre, until the soln. is just acid to dimethyl yellow. The soln. is boiled for $\simeq$ 1 min., 10 ml of 0·01 *N* $BaCl_2$ are added, and the soln. is cooled before adding **I** and, if necessary, 2 ml of 0·01 *N* $MgCl_2$, and titrating with EDTA. (iv) For titration blanks, 10 ml of 0·01 *N* $MgCl_2$ and **I** are titrated with EDTA, a further 10 ml of 0·01 *N* $MgCl_2$ is added and titration is continued to a second end-point. The difference between titres is the titration blank due to impurities in **I**, and the second titre is that appropriate for the standardisation of the EDTA.
S.C.I. ABSTR.

392. **Titration of thiosulphate in boric acid solution.** E. A. Kotsis and V. Bizám (Sulphuric Acid Works, Budapest) (*Magyar Kém. Foly.*, 1955, **61** [1], 17–18).—A thiosulphate soln., acidified with 5 per cent. aq. boric acid (20 to 25 ml for 100 ml of 0·1 *N* $Na_2S_2O_3$), can be titrated directly and accurately with iodine soln. in the presence of starch, even after being set aside for 30 min. The 5 per cent. boric acid can also be used for the acidification of the iodine soln., but not for iodate soln. containing KI, because no iodine is liberated.
A. G. PETO

393. **Reduction of selenous acid by hydrazine sulphate. Volumetric determination of selenium.** B. Suseela (Hindu University, Benares, India) (*Z. anal. Chem.*, 1955, **147** [1], 13–15).—The method depends on the reduction of selenous acid to Se by the addition of an excess of hydrazine sulphate solution, and titration of the unchanged hydrazine with KIO_3 to the iodine monochloride end-point. Results were checked by concurrent gravimetric determination of the Se; reduction is preferably performed by refluxing in 2 to 3 *N* HCl for 15 min. A similar method for determining Te is suggested.
D. R. GLASSON

394. **Photometric determination of a micro amount of tellurium with sodium diethyldithiocarbamate and its application to the analysis of iron and steel.** Hidehiro Gotô and Yachiyo Kakita (*Japan Analyst*, 1954, **3** [4], 299–304).—Tellurium diethyldithiocarbamate can be extracted with benzene from H_2SO_4 soln. (pH 3·3 to 5 *N*). The extinction of the benzene soln. at 436 mμ follows Beer's law for concn. $\geqslant$ 200 μg of Te in 5 ml of benzene. The separation of Te from Fe and constituents of steel, including Bi and Cu (which interfere with the colorimetric determination of Te), can be achieved by precipitating Te with $SnCl_2$ (> 5 g for 0·1 mg of Te in 1 g of sample) in HCl (> 3 *N*) soln. containing $HClO_4$ ($\simeq$ 1 *N*). The time occupied by an estimation is $\simeq$ 2 hr. A similar method can be used for the determination of Te in metals containing Al. *Procedure*—The sample (0·5 to 1 g) is dissolved in dil. HNO_3 (1 + 1) (10 ml), then heated with $HClO_4$ (10 ml) until white fumes are evolved. The product is dissolved in conc. HCl (25 ml) and water (70 ml), heated to boiling point, treated with solid $SnCl_2$ (10 g) and set aside for 1 hr. The ppt. is filtered off, thoroughly washed with 3 *N* HCl and water and dissolved in hot HNO_3 (1 + 1) (5 ml). The soln. is heated with H_2SO_4 (1 + 1) (2 ml) until white fumes are evolved, then cooled and dissolved in water (20 ml). An aq. soln. of Na diethyldithiocarbamate (0·1 per cent) (3 ml) is added to the soln., which is shaken with benzene (5 ml) for 30 sec. The extinction of the benzene layer is measured with a spectrophotometer at 436 mμ.
K. SAITO

395. **Separation of chromium from vanadium with sodium sulphide.** Isamu Tsubaki and Kimimichi Tominaga (*Japan Analyst*, 1954, **3** [3], 242–243).—Tervalent Cr is quant. pptd. with Na_2S soln. containing ammonium acetate at pH 8·4 to 12·0, whilst V^{IV} is not pptd. with the same reagent at a pH of $> 9·0$. The mixed soln. containing Cr''' and VO'' is treated with a saturated aq. soln. of ammonium acetate and Na_2S (10 ml each); the ppt. of Cr is filtered off and washed with dil. Na_2S soln.
K. SAITO

396. **Separation and determination by means of extraction. III. The extraction of molybdenum from hydrochloric acid solution with various organic solvents.** Sakujiro Yamamoto (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [4], 417–423).—The extraction of Mo from 2 to 7 *N* HCl soln. was studied with various organic solvents, including ether, amyl alcohol, butyl acetate, amyl acetate and their binary mixtures. Butyl acetate appears to be the best solvent when used alone; 82·5 per cent. extraction is effected from 5·4 *N* HCl. Mixtures of ether with butyl acetate (1:1), amyl alcohol (1:1) and butanol (1:1) give extractions of > 90 per cent.
K. SAITO

397. **The analysis of binary molybdenum-base alloys.** G. H. Bush and D. G. Higgs (Min. Supply, Armament Res. Est., Sevenoaks, England) (*Analyst*, 1955, **80**, 536–547).—Methods are described for the determination of 15 elements in binary molybdenum-base alloys. The Al is determined by means of 8-hydroxyquinoline; B by a potentiometric titration after removal of Mo; Cr by oxidation and

subsequent titration of the chromate; Co electrolytically after removal of Mo; Cu iodimetrically; Fe by separation as $Fe(OH)_3$, reduction by means of a silver reductor and titration of the reduced Fe; Mn by oxidation and subsequent titration of $KMnO_4$; Ni by electrolysis after separation with dimethylglyoxime; Si by the method commonly used with steel; Ta or Nb by a single pptn. with aq. NH_3, followed by purification of the ppt. with H_2SO_3 and ignition to the oxide; Ti by pptn. with cupferron and ignition to TiO_2; W spectrophotometrically as the thiocyanate; V by a modification of Ridsdale's method; and Zr by separation with cupferron and ignition to ZrO_2. If both Ta and Nb are present, separation is effected by fractional pptn. with tannic acid. Results of analyses of synthetic mixtures are quoted to show the reproducibility attained. A. O. JONES

398. **Quantitative determination of molybdenum in steel by means of chromatographic elution on cellulose columns.** A. M. Ghe and A. R. Fiorentini (*Ann. Chim., Roma*, 1955, **45** [4–5], 400–405).—Molybdenum in steel is determined colorimetrically in quantities $\lessgtr 0{\cdot}05$ per cent., with an accuracy of $\simeq \pm 0{\cdot}02$ per cent., by removing such elements as V, Cr, W, Fe, Co and Cu by chromatography on cellulose columns, followed by treatment with KSCN. A sample of steel (0·25 g) is dissolved in H_2SO_4 (sp. gr. 1·8) (3 ml), which is evaporated off, further acid being added until solution is complete. A mixture (15:15:70, by vol.) (4 ml) of H_2SO_4 (sp. gr. 1·8), H_3PO_4 (sp. gr. 1·71) and H_2O is added, followed, after heating, by a further 5 ml. After being concentrated slightly, the mixture is oxidised with HNO_3 (sp. gr. 1·4) (30 drops), evaporated to about 7 ml, and made up to 10 ml with H_2SO_4. The product is chromatographed in 0·3-ml fractions and eluted with freshly distilled acetylacetone (6 ml). The column is then eluted successively with H_2SO_4 (sp. gr. 1·4) (9 ml); ether (50 ml); aq. KSCN soln. (10 per cent., w/v) (5 ml); $SnCl_2.2H_2O$ soln. (62·5 g in 50 ml of conc. HCl and 200 ml of water) (10 ml). For quant. estimation, the orange-yellow band is separated and dissolved in ether (100 ml) and the extinction coefficient of the resulting solution is measured and compared with standard data.
C. A. FINCH

399. **Colorimetric estimation of uranium with ammonium thiocyanate and its application to the determination of uranium in minerals, particularly monazite concentrates.** M. M. Tillu, D. V. Bhatnagar and T. K. S. Murthy (*Proc. Indian Acad. Sci., A*, 1955, **42** [1], 28–35).—A photometric method, in which NH_4SCN is used, is described for the estimation of U in low-grade ores, after a preliminary separation involving an ether extraction of the nitrates. A rapid method for monazite concentrates is also described. *Procedure*—The monazite concentrate (5 g) is decomposed with 15 ml of conc. H_2SO_4 at 250° C and, when cool, is diluted to 250 ml with ice-cold water. The product, after being set aside for 1 to 2 hr., is filtered, then 5 ml of the filtrate ($\equiv$ 0·1 g of monazite) are treated with 9 ml of 2 *N* H_2SO_4 and 1 ml of $SnCl_2$ reagent (50 g of $SnCl_2.2H_2O$ in 50 ml of conc. HCl, diluted to 250 ml with water). After 5 min., 10 ml of thiocyanate reagent are added (500 g of NH_4SCN in 1 litre). The total extinction, due to U and Ti, is determined at 365 mμ, after adjustment to 100 per cent. transmission with a blank soln. containing no U. The blank soln. is prepared by decomposing a sample of monazite with H_2SO_4, and Th and the rare-earths are separated by precipitation as their oxalates, which are finally ignited to their oxides. This oxide mixture (6·9 g) is heated to fuming with 30 ml of H_2SO_4 and, after the reduction of Ce^{IV}, 2·7 g of P_2O_5 are added (as H_3PO_4) and the soln. is diluted to 500 ml (5 ml $\equiv$ 0·1 g of monazite). Standard curves are constructed from 5 ml of the blank soln. containing 0·5 to 8·0 ml of a standard soln. of U (a 2 *N* H_2SO_4 soln. of UO_2SO_4 containing 0·1 mg of U_3O_8 per ml). A correction for Ti is applied, the amount present being estimated by the peroxide method. It is found that 0·1 mg of TiO_2 gives a coloration similar to that of 0·04 mg of U_3O_8. Up to 125 mg of Th, 4 mg of Fe and 125 mg of P_2O_5 in 25 ml of 2·5 per cent. H_2SO_4 soln., together with Al_2O_3, Mg and lime do not interfere, and SiO_2, Pb and Zn are insol. in 2 *N* H_2SO_4 soln.
G. R. WHALLEY

400. **Separation and identification of acids by paper chromatography. I. The halides.** L. C. Mitchell (Food and Drug Admin., Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [3], 832–835).—A paper is spotted with 0·001-ml portions of 0·1 *M* or 0·01 *M* ammonium, K or Na halides, and developed with a mobile solvent consisting of 5 ml of aq. NH_3 diluted to 100 ml with 2-methoxyethanol. After 4·5 hr., the paper is dried and sprayed with 0·005 *M* $AgNO_3$ (for 0·1 *M*) or 0·0025 *M* $AgNO_3$ (for 0·01 *M*), dried in air and exposed to sunlight. A second paper similarly prepared is treated with 0·0005 *M* alcoholic pyrogallol and dried in air. R_F values for K^+, Na^+, F', Cl', Br' and I' are tabulated. The average R_F values of Cl', Br' and I' show a detectable difference between 0·01 *M* and 0·1 *M* concentrations.
A. A. ELDRIDGE

401. **Determination of fluorine in catalysts containing alumina and silica.** C.-C. Chu and J. L. Schafer (M. W. Kellogg Co., Jersey City, N.J., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1429–1431).—The sample is fused with Na_2O_2 at a low temp. and the AlO_2' and SiO_3'' are pptd. with Zn^{++}. Fluorine ions are distilled as H_2SiF_6 and the distillate is titrated with Th^{++++}.
D. A. PANTONY

402. **Apparatus for the determination of fluorine in solid, liquid or other substances, *e.g.*, calcium fluoride, sodium fluorosilicate, rock phosphates or technical phosphoric acid, by distillation.** E. Tiedemann (Gewerkschaft Victor, Castrop-Rauxel, Germany) (*Z. anal. Chem.*, 1955, **146** [6], 415–416).—A special water vaporiser is designed for conducting a stream of moist air through the distillation apparatus for fluoride determinations. The vaporiser, of treble-jacket construction, is partly immersed in the H_3PO_4 or H_2SO_4 reacting at between 170° and 180° C with the test sample, mixed with powdered glass or sand in a three-necked flask, which carries a dropping funnel for addition of acid, a thermometer, and a wide outlet-tube attached to a condenser. Vaporisation of about 100 to 125 ml of water over 1 to 1·5 hr. suffices for complete removal and condensation of all the HF and H_2SiF_6 vapours.
D. R. GLASSON

403. **Photo-electric end-point determination in the titration of fluorides with thorium nitrate.** R. Mavrodineanu and J. Gwirtsman (*Contr. Boyce Thompson Inst.*, 1955, **18** [3], 181–186).—A photoelectric filter photometer is described for use in the direct titration of fluorides with thorium nitrate soln., with Na alizarinsulphonate as indicator. The instrument is a balance type, with a light source

mounted on an optical bench, and has two lenses, each provided with an iris diaphragm and a coloured gelatin filter with max. transmission at 520 mμ. Two 10-cm glass cells are used of 250-ml capacity, each being connected to a photocell, which is joined in opposition. For the estimation of F, a blank is prepared containing 250 ml of F-free water, the pH is adjusted to 3·0 ± 0·05, 2 ml of a Na alizarin-sulphonate indicator soln. (0·175 g per 500 ml of water) are added and the resulting soln. is added to one of the observation cells. A similar volume of an unknown soln. is added to the other cell, the pH is adjusted, and 2 ml of indicator soln. are added; the optical system is then balanced with the iris diaphragms. The unknown soln. is then titrated with 0·01 *N* $Th(NO_3)_4.4H_2O$ soln. (for 0 to 1000 μg of F), a micro-burette being used. The same optical system is used for a back-titration method. The procedure allows the titration of 1 μg of F in 250 ml of soln. in 10 min. G. R. WHALLEY

404. **A rapid method for the determination of chlorine dioxide in low concentration in air with the aid of a detector tube.** Tetsuzo Kitagawa and Yoshitake Kobayashi (*J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** [3], 177–179).—A small amount of ClO_2 in air (1 to 300 p.p.m.) can be estimated (error $< \pm$ 10 per cent.) by the use of a detector containing *o*-tolidine. Pure silica gel (20 to 40 mesh) is digested with an ethanolic soln. of *o*-tolidine containing a small amount of HCl, then dried and packed in a glass tube (0·3 g, length of the column 6 to 8 cm). The sample (100 ml) is passed through this tube ($\simeq$ 50 sec.) and the length of yellowish zone is measured. The logarithm of the length (mm) is proportional to the logarithm of the concn. of ClO_2 up to 300 p.p.m. The presence of oxidising agents such as Cl, NO_2, O_3, Br and H_2O_2 interferes with the estimation. K. SAITO

405. **Determination of chlorine dioxide concentration in air by the gas-electrode method.** Kanichi Ogawa and Teruhiko Naito (*Japan Analyst*, 1954, **3** [5], 421–423).—In a new method for the continuous determination of the concn. of ClO_2 in air the use of the following cell is suggested: $ClO_2(Pt) - ClO_2' \| KNO_3 \| KCl \| Hg_2Cl_2 - Hg$. A saturated soln. of $AgClO_2$ is bubbled with the sample gas to produce a half-cell of ClO_2'. When the e.m.f. is plotted against the concn. of ClO_2 in air, a straight line is obtained for the range 0·5 to 10 per cent. Chlorine in air must be converted into an equiv. amount of ClO_2 by bubbling it through a saturated soln. of $AgClO_2$ before being introduced to the cell. The presence of chlorine thus results in values that are too high when the content is more than 1 per cent. of the ClO_2. The cell must be kept in a thermostat during the e.m.f. measurement. K. SAITO

406. **Application of the two-stage ascorbic acid - iodate titration to the determination of iodine and iodide.** G. S. Deshmukh and M. G. Bapat (Hindu Univ., Benares, India) (*Z. anal. Chem.*, 1955, **147** [4], 271–273).—Iodine and iodide are estimated in the presence of each other by a two-stage titration with KIO_3 after the addition of ascorbic acid. A known excess of ascorbic acid, previously standardised against KIO_3, is added to the iodine - iodide mixture, and the excess is titrated with KIO_3 in $\simeq$ *N* HCl soln. The acidity is raised to 4 *N* HCl, and all the iodide is converted into ICl with more KIO_3. The difference between the standard and back-titrations for the first end-point gives a measure of free I, whilst the titration difference for the second end-point gives a measure of the total I + I′ content, allowance being made for the change of equivalence of the KIO_3 with acidity. J. H. WATON

407. **Electrometric determination of iodides based on the polarisation of the electrode.** E. Michalski and M. Zuk-Kunaszewska (*Łódz Towarz. Nauk, Section III*, 1954, No. 34, 16 pp.).—A solution of an iodide to be titrated is connected by a bridge of KNO_3 with a satd. $HgNO_3$ soln. Immersed in each soln. are platinum electrodes, connected through a galvanometer. A small current is registered which is due to the reaction $2I' \rightleftharpoons I_2 + 2e$. As the iodide soln. is titrated with $AgNO_3$ the iodide concn. decreases because of the formation of AgI, and the current drops. At the equivalence point a sudden fall in the concn. of iodide produces polarisation, and the current stops. Iodide solutions of 0·004 to 0·1 *N* can be determined with a mean error of 0·05 per cent. Errors of 0·2 and 1 per cent., respectively, are obtained in the presence of chlorides and bromides. CHEM. ABSTR.

408. **The volumetric determination of manganese with potassium ferrocyanide.** I. Sajó (Vasipari Kutato, Budapest) (*Magyar Kém. Foly.*, 1955, **61** [7], 196–198).—In the presence of NH_4Cl, Mn is quant. pptd. by $K_4Fe(CN)_6$; the ferrous - ferricyanide redox system indicates the end-point; 3:3′-dimethylnaphthidine (**I**) is red in the presence of $K_3Fe(CN)_6$, but colourless in $K_4Fe(CN)_6$. A modified method describes the simultaneous determination of Al and Fe; these form a stable complex at pH 3; Ti, Ca, Mg, etc., do not interfere. *Procedure*—To a soln. containing 5 mg of Mn, add NH_4Cl (5 g) and neutralise to Congo-red paper. Add 5 ml of buffer [chloroacetic acid (100 g) and NaOH (25 g) in 1 litre of H_2O], 1 per cent. $K_3Fe(CN)_6$ (0·5 ml) and 0·5 per cent. **I** in acetic acid (8 to 10 drops). Titrate slowly with 0·05 *M* $K_4Fe(CN)_6$ (standardised against zinc or manganese soln.) until colourless. If Al and Fe are present, add NH_4Cl and adjust the pH as above. If > 10 mg of Fe are present, add glacial acetic acid (7 ml) and then aq. NH_3 dropwise, until one drop turns the soln. red. Then add the buffer and 20 per cent. sulphosalicylic acid soln. (2 ml); warm the soln. to between 40° and 50° C and titrate the Fe^{III} with 0·05 *M* disodium EDTA. Add excess of disodium EDTA and titrate the Mn as above. Remove the manganese ferrocyanide ppt. by centrifuging, add aq. NH_3 (4 ml, d = 0·91) and back-titrate the excess of EDTA with Zn acetate (*cf.* Sajó, *Anal. Abstr.*, 1955, **2**, 1474); this gives the content of Al. **I** acts as indicator. By this method, Mn, Al and Fe can be determined in 8 to 10 min.; it is also suitable for manganese ores. A. G. PETO

409. **Flame-photometric determination of manganese.** W. A. Dippel and C. E. Bricker (Princeton Univ., Princeton, U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1484–1486).—Manganese is determined by a normal flame-photometric procedure, the intensity at 403·3 mμ with respect to background intensity at 400 and 406 mμ being chosen for measurement. D. A. PANTONY

410. **Rapid determination of manganese in metal alloys. II. Photometric evaluation of the perchloric - phosphoric acid method.** H. Schröder (*Metall*, 1955, **9** [3–4], 100–102).—The method described depends on the fact that Mn^{++} is oxidised to Mn^{+++} with $HClO_4 - H_3PO_4$. The absorption due to Mn^{+++} and any other coloured ion in the solution is

measured at 465 mμ. Ferrous ammonium sulphate is then added in order to decolorise the $Mn^{\cdots}$, and the absorption is re-measured. The difference between the absorption readings bears a relationship to the content of Mn. The method is used to advantage when no potentiometric titration set-up is available and, in many cases, separation from accompanying metals is unnecessary, although V interferes. C. J. KEATTCH

411. **Spectrometric determination of rhenium and its separation from molybdenum.** R. J. Meyer and C. L. Rulfs (Univ. Michigan, Ann Arbor, Mich., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1387–1389).—Rhenium is converted into perrhenate and the Mo is separated by extraction of its cupferron complex with ether. After reduction with hydrazine in HCl soln., the concn. of Re is measured spectrophotometrically at 281·5 mμ. A precision of ± 2 per cent. is given. D. A. PANTONY

412. **Volumetric determination of iron by reduction with hypophosphite.** M. N. Sastri and C. Radhakrishnamurti (Andhra Univ., Waltair, S. India) (*Z. anal. Chem.*, 1955, **147** [1], 16–18).—A method for the reduction of Fe^{III} to Fe^{II} with hypophosphite is proposed. The iron solution is boiled for 15 to 20 min. with an excess of sodium hypophosphite (5 per cent.) in aq. HCl (overall concn. 2 *N*). The Fe^{II} in the cooled solution is titrated with standard sodium vanadate or $Ce(SO_4)_2$, N-phenylanthranilic acid being used as indicator. D. R. GLASSON

413. **Use of some new chelating agents for the colorimetric determination of iron. I. Ethylenediaminebissulphosalicylaldehyde [di(sulphosalicylidene)ethylenediamine].** A. K. Mukherjee (Indian Association for Cultivation of Sci., Calcutta, India) (*Anal. Chim. Acta*, 1955, **13** [3], 268–272.—From 0·25 to 10 μg of $Fe^{\cdots}$ can be determined spectrophotometrically from the absorption at 510 to 520 mμ of the stable violet - red complex formed by chelation of $Fe^{\cdots}$ with di(sulphosalicylidene)-ethylenediamine (1 per cent. solution). Measurements should be made at a pH between 2·8 and 5·5, and ≃ 35° C. The ions HPO_4'', BO_3'', MoO_4'' and F' interfere strongly, and other ions to a less extent. The sensitivity is ≃ 0·1 μg per sq. cm of the cell. **II. 5-Aminosalicylic acid (sodium salt).** (*Ibid.*, 1955, **13** [3], 273–276).—From 0·05 to 15 p.p.m. of $Fe^{\cdots}$ can be determined spectrophotometrically from the absorption at 450 to 500 mμ and pH 1·5 to 3·05, or 3·4 to 5·05, of the stable coloured complex formed by the reaction between $Fe^{\cdots}$ and the sodium salt of 5-aminosalicylic acid (1 per cent. solution). Uranyl ions should be absent, and Cu, Ni, Co, HPO_4'', BO_3'', CrO_3'', MoO_4'' and F' interfere strongly. The sensitivity is ≃ 0·05 μg. W. J. BAKER

414. **The colorimetric micro-determination of ferric iron by means of an activated reaction.** G. Almássy and M. Z. Kávai (*Magyar Kém. Foly.*, 1955, **61** [8], 246–248).—In the presence of 2:2′-dipyridyl, the normal potential of the Fe^{II} - Fe^{III} system is sufficient to oxidise aniline in neutral or faintly acid soln. The Fe^{II} - dipyridyl complex is red; oxidised aniline is violet - red. *Procedure*—To 10 ml of an acid soln. (≯ 0·1 *N*) containing ≯ 20 μg of Fe, add 0·5 ml of aniline soln. (10 ml of redistilled aniline + 75 ml of redistilled 20 per cent. HCl + 15 ml of H_2O) and one drop of bromophenol blue (0·1 g in 1 litre of ethanol). The pH is adjusted to 4·7 with 15 per cent. Na acetate soln. Add 0·2 m of dipyridyl reagent (0·75 g in 100 ml of ethanol); heat at 100° C for 5 min., cool and dilute to 15 ml. The extinction is measured in a Pulfrich photometer (S50 filter, 5-cm cell). The Beer - Lambert law is obeyed. The calibration curve is determined similarly. The content of Fe^{III}, even of A.R. reagents, must be taken into account. The largest admissible amounts of foreign ions are discussed, but even lower concn. increase the reaction times. The sensitivity is 0·03 μg of Fe^{III} per ml. A. G. PETO

415. **A rapid determination of ferrous oxide in chromite.** Tadashi Nagaoka and Seiichi Yamazaki (*Japan Analyst*, 1954, **3** [5], 408–409).—The method for determining FeO with the aid of V_2O_5 (Schein, *Zavod. Lab.*, 1937, **6**, 1199) was applied to the analysis of chromite. The sample (0·25 g, for < 25 per cent. of FeO) is heated with a mixture (30 ml) of H_3PO_4 and H_2SO_4 containing V_2O_5 (1 g in 100 ml of conc. H_3PO_4 and 200 ml of conc. H_2SO_4) until white fumes are evolved. The product is diluted with water (250 ml) and titrated with $KMnO_4$ (0·1 *N*). The influence of the intense green colour of $Cr^{\cdots}$ can be eliminated by adding $Co^{\cdot\cdot}$ (3 times the weight of the Cr). The V_2O_5 soln. must be treated with $KMnO_4$ before use until a very faint colour of MnO_4' remains. The deviation is ≃ 0·4 per cent. (absolute value). K. SAITO

416. **Application of organic solvent extraction to flame spectrophotometry. Determination of iron in non-ferrous alloys.** J. A. Dean and J. H. Lady (Univ. Tennessee, Knoxville, Tenn., U.S.A.) (*Anal. Chem.*, 1955, **27** [10], 1533–1536).—The determination of Fe by flame photometry is subject to interference from a number of extraneous elements in non-ferrous alloys. This difficulty can be largely overcome by selective extraction from aqueous solutions of pH 0·5 to 1·0 with acetylacetone, which serves both as chelating agent and solvent for Fe. The solvent extract can be aspirated directly into an oxy-acetylene flame, the luminescence of the Fe 3720-A line being increased sixfold by the presence of the acetylacetone. No interferences were found when this method was applied to aluminium-, copper-, and nickel-base alloys and to limestone, except when Cu was present in a final concentration > 1 per cent. The standard deviation of replicates was ± 3 per cent. K. A. PROCTOR

417. **Spectrographic estimation of iron, titanium and antimony in glass.** W. Ward and D. D. Innes (*J. Soc. Glass Tech.*, 1955, **39** [188], T156–161).—The Hilger E492 (slit 0·015 mm × 10 mm) is used with a band setting of 3500 to 2450 A and the internal standard line pairs Fe 3021·07 - Co 3013·6, Ti 3242·0 - Co 3237·0 and Sb 2598·1 - Bi 2627·9. *Procedure*—A mixture (50 mg) of C, 92·5, Bi_2O_3, 5, and Co_2O_3, 2·5 per cent., is mixed with 100 mg of finely ground sample and packed in a hole 2·4 mm × 4 mm deep in the end of the electrode. Excitation is with 10 amp. at 240 V for 3·5 min. (gap 10 mm). The "Chromatic" plate (wave-band setting 3500 to 2450 A) is developed in I.D.2 and the line densities are measured with a Hilger non-recording microphotometer. The analysis is completed in 1·5 hr. with percentage coeff. of variation of 5·58, 3·43 and 3·33 for TiO_2, Sb_2O_3 and Fe_2O_3, respectively. J. A. SUGDEN

418. **The spectrographic determination of phosphorus and carbon in steel by the profile method.** R. Breckpot and Z. Hainski (Univ. Louvain,

Belgium) (*Mikrochim. Acta*, 1955, [2–3], 646–656).—The use of a recording quartz-prism spectrograph with a continuous arc source is described for the determination of several elements (Mn, C, P, Si) in steel. The dispersion of the instrument in the far ultra-violet is twice that of one in which a grating of 36,000 lines per inch is used, and the luminosity is ten times as great. The increased dispersive power facilitates the positioning of the photocells. The entrance slit is fitted with a slow back-and-forth lateral movement, of amplitude 0·1 mm, which results in a lateral displacement of the spectrum and removes the necessity for critical and permanent alignment of the exit slit. It is possible by this method to separate lines as close as Fe 2136·55, P 2136·19 and Cu 2135·98 A. It has also been shown that the use of a Feussner-type spark source obviates the use of an internal standard. Samples for analysis in the form of pencils, 10 mm in diam., are prepared by hot-forging the bottom of an ingot previously quenched in Al, and are finished by sectioning, turning and machining.

K. A. PROCTOR

419. **Acid contamination as a source of error in boiling nitric acid test for corrosion-resistant steel.** R. J. Bendure (*Bull. A.S.T.M.*, 1955, **207**, 76–77).—In applying the boiling HNO_3 test (A.S.T.M. Standard A262–52T) for determining the quality of stainless steel, high and erratic penetration rates (in. per month) can be obtained when the HNO_3 contains fluorides and high humidities are maintained under the hood. The HF vapour attacks the specimen. Contamination from H_2S used in the vicinity should also be avoided.

W. J. BAKER

420. **Colorimetric analysis with organic reagents. III. Colorimetric determination of cobalt with 1-nitroso-2-naphthol by an extraction method.** Nobuichi Oi (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [4], 413–416).—Experimental conditions for the extraction of the Co - 1-nitroso-2-naphthol complex with various organic solvents were examined with reference to the pH value of the aq. soln., the time necessary for the formation of the complex, and the removal of the excess of 1-nitroso-2-naphthol (**I**). In the presence of a slight excess of **I** the reaction between Co and **I** is complete within 10 min. in a bath of boiling water. When the aq. layer is treated with 6 *N* NaOH (2 ml), the excess of **I** is not extracted with $CHCl_3$, whereas the extraction of the Co - **I** complex is not affected. Another advantage of this treatment is that the complexes of **I** with Cu or Fe are decomposed in alkaline soln.

K. SAITO

421. **Cobalt (III) oxidimetry.** C. E. Bricker and L. J. Loeffler (Princeton Univ., N.J., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1419–1423).—Solutions of $Co^{\cdots}$ in dil. H_2SO_4 are prepared electrolytically and are examined as possible titrants for the determination of $Fe^{\cdot\cdot}$, $Fe(CN)_6^{\prime\prime\prime\prime}$, $Ce^{\cdots}$, $AsO_3^{\prime\prime\prime}$, oxalate and peroxide, end-points being found spectrophotometrically.

D. A. PANTONY

422. **Chemical analysis by the use of catalysed or induced reactions. V. Micro-determination of cobalt and iron by induced precipitation with zinc mercury thiocyanate complex.** Shukichi Sakuraba (*Japan Analyst*, 1954, **3** [5], 417–420).—Cobalt (< 120 μg) and Fe (< 60 μg) can be quant. co-pptd. with Zn ($\simeq 30$ mg) by treatment with $(NH_4)_2Hg(SCN)_4$ (15 per cent.) (3 ml per 20 ml of the sample soln.). The ppt. is dissolved in a mixture of acetone and methanol (1 + 1) (5 ml) containing NH_4SCN (10 per cent.) and the extinctions are measured at 480 mμ (max. absorption of Fe - SCN complex) and 620 mμ (max. absorption of the Co complex); these are in accord with Beer's law for up to 60 μg of Fe and 150 μg of Co per 5 ml, respectively. For the determination of Co in the presence of Fe or Cu, one drop of NH_4F (10 per cent.) is added to the org. layer. The determination of Fe is vitiated by $Cu^{\cdot\cdot}$ (> 20 μg) and $Cr_2O_7^{\prime\prime}$ (> 50 μg). No interference results from other ions, including $WO_4^{\prime\prime}$, $CrO_4^{\prime\prime}$, $Ni^{\cdot\cdot}$ and $MnO_4^{\prime}$.

K. SAITO

423. **The determination of small amounts of nickel in copper ores and concentrates containing iron and cobalt.** A. Liberman (RhoAnglo Mine Services, Kitwe, N. Rhodesia) (*Analyst*, 1955, **80**, 595–598).—Under controlled conditions of acidity the blue compound that Co forms with HCl is strongly adsorbed on anion-exchange resins and Fe is also completely exchanged. Nickel can thus be separated from Co and Fe in one operation. The solution of the ore in HNO_3 - $HClO_4$, after removal of $HClO_4$ by fuming, is treated with H_2S to remove the metals of group 2 together with SiO_2. The filtrate is made 8 *N* with respect to HCl and passed through the anion-exchange column (Amberlite IRA, De-Acidite FF or Dowex I). After removal of HCl from the eluate by evaporation or distillation, and fuming with HNO_3 - $HClO_4$, the volume is adjusted and Ni is determined absorptiometrically by the hypobromite - dimethylglyoxime method, the colour being measured at 455 mμ or in a Spekker absorptiometer with an OB1 filter. The calibration graph is prepared from standard solutions of Ni subjected to the same colorimetric procedure. The method has been applied to sulphide and oxide copper ores and their concentrates with satisfactory results.

A. O. JONES

424. **Coulometric determination of nickel and cobalt.** J. J. Lingane and J. A. Page (Harvard Univ., Cambridge, Mass., U.S.A.) (*Anal. Chim. Acta*, 1955, **13** [3], 281–287).—From 10 to 100 mg each of nickel and cobalt can be determined successively in 100 ml of solution by controlled potentiometric coulometry; a mercury cathode is used, with aq. 1 *M* pyridine plus 0·05 *M* KCl as electrolyte. A platinum auxiliary anode depolarised by hydrazine is preferable to an Ag - AgCl anode. The control potentials for deposition and separation of the metals are $-0{\cdot}95$ V *vs.* the S.C.E. for nickel and $-1{\cdot}20$ V for cobalt; the pH should be between $\simeq 6{\cdot}3$ and 7·2. One successive determination takes from 4 to 6 hr., and the error is $\pm$ 0·5 mg.

W. J. BAKER

425. **Use of oscillographic polarography in quantitative analysis. III. Determination of nickel and detection of copper and iron in cobalt salts.** J. Doležal and P. Hofmann (Ústav pro chem. anal. Karlovy Univ., Prague, Czechoslovakia) (*Chem. Listy*, 1954, **48** [11], 1610–1615).—Though less accurate than classical polarography, oscillographic polarography constitutes a rapid method for the routine determination of Ni in cobalt salts. Copper, Fe, Cd, Pb, Zn and Tl may be present, but $UO_2^{\cdot\cdot}$ and much As interfere. A new micro-vessel (3 to 5 ml in vol.) for the mercury-jet electrode is described. *Procedure*—To an approx. *M* soln. of the cobalt salt (2 ml) add 2 *M* $K_4P_2O_7$ (5 ml) and 2 *M* ethylenediamine tartrate (1·25 ml), and dilute the soln. with H_2O to 10 ml. Treat similarly a *M* soln. of the nickel-free cobalt salt. Titrate the latter

comparison soln. with 0·01 *M* $NiSO_4$ until the polarographic curves of both soln. on the oscillographic screen coincide. G. GLASER

426. **EDTA titration of palladium and gold in presence of platinum.** Outokumpu Oy (Metalworks, Pori, Finland) (*Chemist Analyst*, 1955, **44** [1], 11–12).—The method described for the determination of Pd in soln. containing Pd, or in double salts of Pd and Pt, is based on the EDTA titration of Ni displaced from $K_2Ni(CN)_4$ by Pd, Eriochrome black T being used as indicator. If Au is present, it will be titrated at the same time. A similar procedure can be adopted for the determination of Au in alloys and in platinum metal, after first removing Ag as chloride. In a method for the direct titration of Pd, even in the presence of Pt, a chlorine-free acidic soln. is treated with an excess of EDTA (disodium salt), followed by titration with bismuth nitrate in the presence of catechol violet as indicator, and back-titration of the excess of EDTA. O. M. WHITTON

427. **Colorimetric determination of platinum with stannous chloride.** O. I. Milner and G. F. Shipman (Socony Mobil Oil Co., Inc., Paulsboro, N.J., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1476–1478).—Conditions for the production of a stannous - platinum chloride complex are examined, with a view to the colorimetric determination of Pt. A 1·5 to 2·5 *N* HCl soln. is a satisfactory medium. D. A. PANTONY

428. **Applicability of a colorimetric determination of platinum in platinised catalysts.** F. Wagner (Scholven-Chemie AG, Gelsenkirchen-Buer, Germany) (*Z. anal. Chem.*, 1955, **147** [1], 18–20).—The Pt (≃ 5 mg) is completely separated from its alumina carrier (1 g) by preliminary ignition for 30 min. at 1100° to 1150° C, to convert the Al_2O_3 into its α-form (corundum), and then dissolution by heating for 10 min. with water (2 ml) and conc. H_2SO_4 (5 ml), followed by dilution with 12 ml of water and reheating with conc. HCl (1 ml) and 100-vol. H_2O_2 (0·5 ml). After the resulting solution has been made up to 250 ml, the Pt, in aliquot portions, is colorimetrically determined by treatment with conc. aq. NH_4Cl, conc. HCl and 2 *M* $SnCl_2$ (the final concn. being 1 *M*, 1·7 *M* and 0·2 *M*, respectively), the absorption being measured at 400 mμ. The relative deviation from the reference curve (for pure Pt) is ± 0·2 per cent. The accuracy is better than ± 0·002 per cent. of Pt. D. R. GLASSON

429. **Determination of wolframite in scheelite.** S. Kallmann (Ledoux & Co., Inc., Teaneck, N.J., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1433–1435).—The sample is dissolved in dil. HCl in the absence of oxidising agents, and the resulting Fe^{II} derived from the wolframite is determined by standard methods. D. A. PANTONY

See also Abstracts 322, 325, 326, 327, 328, 332, 335, 443, 472, 473, 604.

3.—ORGANIC ANALYSIS

430. **A modified Unterzaucher method for the direct determination of combined oxygen.** F. H. Oliver (Imp. Coll. Sci. Tech., London) (*Analyst*, 1955, **80**, 593–594).—A modified method is described for the determination of combined oxygen in compounds that may also contain S. As recommended by Oita *et al.* (*Anal. Abstr.*, 1954, **1**, 1859), a roll of copper gauze heated to 900° C is used to retain the S, and a carbon - platinum mixture (1 + 1) converts the O from the compound into CO at 900° C instead of the usual 1200° C. Only one furnace is necessary. The procedure adopted is that of Unterzaucher (*Brit. Abstr. C*, 1953, 116), with the modification that the boat is left at the entrance of the furnace during the sweeping-out period and is brought into position by external application of a magnet to a glass-covered iron bar behind the boat. The preparation of the reagents is described and results are given for a variety of compounds analysed by the method. A. O. JONES

431. **Volumetric determination of sulphur in organic compounds.** Nobuhiko Iritani and Yoshimasa Tanaka (*Kumamoto Pharm. Bull.*, 1955, [2], 30–32).—A new method for the semi-micro and micro-determinations of sulphur in organic substances is described. The sample (20 mg) is heated in a sealed tube with 1 ml of fuming HNO_3 at 250° C for 5 hr. On being cooled, the contents are removed to an evaporating dish on a water bath to remove traces of HNO_3. The residue is dissolved in water, and a few drops of 15 per cent. NaOH and 0·1 per cent. phenol red soln. are added. The soln. is then neutralised with 10 per cent. acetic acid to a yellow colour and titrated with 0·05 *N* $BaCl_2$ soln. The titration is continued until the colour of Na rhodizonate paper changes to red; the indicator blank under the same conditions is subtracted from the titration figure. The maximum error recorded was 0·26 per cent. In micro-estimations, samples of 5 to 8 mg were used and 0·02 *N* $BaCl_2$ soln. The max. error recorded for these was 0·25 per cent. Back-titration of a given excess of $BaCl_2$ added to the sulphate soln. gives a large error. R. S. TONKS

432. **An improved procedure for the micro-determination of the N-methyl group.** Takeo Sudo, Daizo Shimoe and Takatomo Tsujii (*Japan Analyst*, 1954, **3** [5], 403–408).—A modification for the improvement of Furter's double-distillation method for the determination of N-methyl groups (*Helv. Chim. Acta*, 1938, **21**, 1144) is suggested. Attempts were made to remove the iodine vapour and the excess of HI, which are produced on the conversion of N-methyl groups into quaternary ammonium salts with HI, by bubbling through a $Na_2S_2O_3$ soln. This modification resulted in the decrease of the error to ± 0·3 per cent. K. SAITO

433. **The determination of acetylene and aldehyde in ethylene oxide.** V. W. Reid and D. G. Salmon (Petrochemicals Ltd., Urmston, Manchester) (*Analyst*, 1955, **80**, 602–603).—The determination of both acetylene and acetaldehyde in ethylene oxide is described. The ethylene oxide is delivered from a pipette calibrated for weight into a cooled 0·1 per cent. soln. of Na_2SO_3 and, after 5 min., the soln. is titrated with 0·1 *N* iodine to the starch end-point, the titre being noted. Solid $NaHCO_3$ is then added and the titration is continued. The difference between the two titres, corrected by deduction of the corresponding difference in a blank determination, is equivalent to the acetaldehyde content. Acetylene is determined colorimetrically with the reagent of Geissman *et al.* (prep. described), the colour being evaluated spectrophotometrically at 550 mμ or with a Spekker absorptiometer with an Ilford OG1 filter. Calibration graphs are

prepared from gaseous acetylene in glass sampling-tubes, the reagents being forced into the tubes in the manner described by Geissman *et al.* (*Anal. Chem.*, 1947, **19**, 919). A. O. JONES

434. **The colorimetric determination of trace amounts of alcohols.** V. W. Reid and D. G. Salmon (Petrochemicals Ltd., Urmston, Manchester) (*Analyst*, 1955, **80**, 704–705).—In the method described by Reid *et al.* (*Brit. Abstr. C*, 1952, 437) for determining alcohols in dil. aq. soln. in the 0 to 5 per cent. region, the max. sensitivity of colour evaluation was not obtained over the range of colours produced by very dil. alcoholic soln. The determination of alcoholic contents below 0·1 per cent. is now described. The $Ce(NO_3)_4.2NH_4NO_3.2H_2O$ reagent is prepared and standardised as previously described (*loc. cit.*). The sample (10 ml) is mixed in a 4-cm cell with 4 ml of the reagent and, after 5 min., the extinction is measured at 486 mμ against a reference cell of the reagent and distilled water. The calibration graph for each alcohol is most conveniently prepared on a w/v basis. The accuracy attainable is $\simeq \pm$ 0·2 mg of alcohol ($\pm$ 20 p.p.m.). To apply the method to the determination of trace amounts of alcohol in hydrocarbon solvents the extinction of an aq. extract of the sample is measured. The accuracy is $\pm$ 1 p.p.m. Results are given of determinations of methanol, ethanol and *iso*propanol in aq. soln. and of methanol in *iso*octane. A. O. JONES

435. **Analytical determination by density method. Determination of ratio of mixtures of liquids [organic] and water.** J. Takanaka (*J. Sci. Hiroshima Univ., A*, 1955, **18** [3], 413–418).—Density measurements in the approx. temp. range 10° to 50° C are reported for ethanol, acetic acid, and a series of their aq. solutions. The constants of a linear density-temp. relation for each system and of a three-constant log (density) - concentration relation at constant temperature are tabulated. A. JOBLING

436. **Paper electrophoresis of polyhydric alcohols.** D. Gross (Tate and Lyle, Ltd., Keston, Kent, England) (*Nature*, 1955, **176**, 362–363).—The high-voltage electrophoresis technique (Gross, *Nature*, 1953, **172**, 908, and 1954, **173**, 487) can be applied to the separation of mixtures of polyols as sugar - borate complexes. In particular, analysis of mixtures of mannitol, sorbitol and dulcitol in the presence of erythritol is possible. Other polyhydric alcohols investigated include mannose, sorbose, glucose, fructose, ethanediol and glycerol. Glyceraldehyde and dihydroxyacetone, with very similar mobilities, could not be separated, but chromatographic methods are available. The advantage claimed is short time of operation (1·5 to 3 hr.). Experimental requirements are a potential gradient of 40 to 80 V per cm, with a soln. of polyols in 0·05 *M* sodium borate buffer (pH 9·2). A soln. of lead tetra-acetate (1 per cent.) in benzene is employed as a spraying reagent. D. G. FORBES

437. **Glycerine (glycerol).** British Standards Institution (2, Park St., London) (B.S. 2621–5: 1955, 58 pp.).—Specifications cover five grades of glycerin: soap-lye crude glycerin (2621); saponification (hydrolyser) crude glycerin (2622); pale-straw glycerin (2623); dynamite glycerin (2624) and chemically pure glycerin (2625). These specifications replace those given in the International Standard Methods for crude glycerin (1911). The major changes are the inclusion of an arsenic limit on commercial crude glycerin; the deletion, after July 1956, of the dichromate and acetin methods of estimation; the introduction of the sodium periodate method of assay; the introduction of the Karl Fischer method for water determination (B.S. 2511) and a modification to the non-volatile residue test. Additional methods are given in an appendix. H. B. HEATH

438. **Analysis for industry. [Determination of aldehydes and ketones.]** J. G. P. Farr (*Ind. Chem. Mfr*, 1955, **31** [368], 464–466).—Analytical methods for the determination of aldehydes or ketones or both, involving the use of (1) bisulphites, (2) compounds of Hg (*e.g.*, Nessler's reagent or $HgSO_4$), (3) oxidation of formaldehyde, (4) argentimetric methods, or (5) hypoiodites, are reviewed. (101 references.) S.C.I. ABSTR.

439. **New method for the colorimetric determination of formaldehyde.** K. Dušek and S. Hudeček (Výzkumný ústav syntetických pryskyřic, Pardubice, Czechoslovakia) (*Chem. Listy*, 1954, **48** [11], 1628–1633).—A new reagent for the colorimetric determination of formaldehyde, possessing a number of advantages over Schiff's reagent, is prepared as follows. Crystalline Na_2SO_3 (12·1 g) is dissolved in a soln. of methyl violet (0·5 g) in H_2O (400 ml) containing conc. HCl (5 ml). After more conc. HCl (5 ml) has been added, the soln. is diluted to 500 ml, set aside for 8 hr., then treated with activated charcoal (0·5 g) and, after 5 min., is filtered. The almost colourless reagent forms with formaldehyde a colour with an absorption max. at $\simeq$ 578 mμ. The extinction curve of the new reagent, unlike that of Schiff's, is linear for a certain concn. range of formaldehyde (0·09 to 0·44 mg per ml). Formaldehyde can be determined after 1 hr. in the presence of a 2 to 3-fold excess of acetaldehyde at a pH as high as 3. G. GLASER

440. **A new method for determination of glyoxal.** F. Becke and O. Gross (Badischen Anilin- und Soda-fabrik, Ludwigshafen, Germany) (*Z. anal. Chem.*, 1955, **147** [1], 9–12).—Glyoxal is determined by pptn. as its Schiff's base with *cyclo*hexylamine. Test solutions (0·1 to 0·2 g of glyoxal in 50 ml of water) are neutralised with 0·1 to 0·5 *N* NaOH, thymol blue being used as indicator, and then shaken for 10 to 15 min. with 0·5 *N* *cyclo*hexylamine (25 ml). After the ppt. has been washed with water (200 to 300 ml), the excess of *cyclo*hexylamine in the filtrate is titrated with 0·1 *N* HCl. Glyoxal can be determined in the presence of glyoxylic acid by this method. D. R. GLASSON

441. **Polarography of saturated acids and unsaturated fatty acids that have double bonds in positions other than the α - β position.** Senjiro Maruta and Fumio Iwama (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [5], 548–551).—Polarographic reduction waves of a number of saturated acids and unsaturated fatty acids that have double bonds in positions other than the α - β position (not conjugated with the double bond of the carboxyl group) were observed in aq. acetone (5 to 20 per cent.) containing LiCl (0·1 mole per litre) as the supporting electrolyte. The half-wave potentials of these acids are $-1{\cdot}87 \pm 0{\cdot}04$ V *vs.* the S.C.E., and are practically independent of the length of the carbon chain, *e.g.*, $-1{\cdot}88$ for acetic acid, $-1{\cdot}86$ for lactic acid, $-1{\cdot}85$ for palmitic acid, and $-1{\cdot}90$ for oleic acid. The wave heights are proportional to the concn. of the acids for soln. up to

$6 \times 10^{-3} M$; the specific height (per millimole), however, decreases with increase in molecular weight, presumably owing to decrease of the diffusion constant. The esters of these acids do not give polarographic waves under the given conditions, and do not interfere with the polarographic reduction of solutions containing fatty acids. The polarographic method appears to be suitable for the determination of free fatty acids in esters. K. SAITO

442. **Titration of weak acids in non-aqueous media.** K. Backe-Hansen (Statens Farmakopélaboratorium, Oslo, Norway) (*Med. Norsk Farm. Selsk.*, 1955, **17** [6], 282–291).—A comprehensive review is given of early and present work on the titration of weak acids in non-aqueous media, together with a brief account of the underlying theory. The merits of various indicators are described, magneson (*p*-nitrophenylazoresorcinol) being recommended to give a sharp end-point in ethylenediamine, butylamine and dimethylformamide. The increasing significance of the subject in pharmaceutical chemical analysis is stressed. (52 references.) P. HAAS

443. **Determination of tartrate in copper cyanide baths.** O. A. Ohlweiler and J. O. Meditsch (Escola de Engenharia, P. Alegre, Brazil) (*Chemist Analyst*, 1955, **44** [1], 19–20).—The sample is neutralised to phenolphthalein with H_2SO_4 and 10 per cent. $AgNO_3$ soln. is added, dropwise, until the ppt. of argentocyanide changes from white to grey. When pptn. is complete, the ppt. is filtered off, and the filtrate, after oxidation with $KMnO_4$, is back-titrated with $Na_2S_2O_3$ soln. The use of nitrobenzene to coagulate the ppt. has been found unnecessary. O. M. WHITTON

444. **Separation of mannose from a mixture of sugars by paper chromatography.** K. Krishnamurthy and M. Swaminathan (Centr. Food Techn. Res. Inst., Mysore, India) (*J. Sci. Ind. Res., B, India*, 1955, **14** [6], 310–311).—An investigation was made to find a suitable solvent mixture for the separation of mannose from other sugars. The best of the mixtures tested was prepared by shaking together phenol, *n*-butanol, glacial acetic acid and water (20:20:8:40, by vol.) and allowing the mixture to separate. The upper layer was used for irrigating the chromatograms. Whatman No. 1 filter-paper sheets, buffered at pH 2·0, were employed. After being irrigated for 72 hr., the chromatograms were air-dried (45° to 50° C) and sprayed with benzidine-trichloroacetic acid reagent for identifying sugar spots, and then heated at 80° C for 10 min. to develop the colours. The method is also suitable for the identification of arabinose. G. C. JONES

445. **Reversion of saccharides and its significance for the analysis of carbohydrates. II. Constitutional and analytical studies.** K. Müller and K. Täufel (Inst. Ernähr., Potsdam-Rehbrücke, Ger.) (*Z. LebensmittUntersuch.*, 1955, **100** [6], 437–441).—The constitution and chemical properties of reversion products, especially oligosaccharides of glucose, are discussed on the basis of recent literature and the authors' experiments. It is shown that the reversion of monosaccharides, occurring during acid hydrolysis of oligo- and poly-saccharides, interferes with the desired total cleavage and may thus lead to errors in the analysis of saccharides. This reversion and its consequences are avoided when acid hydrolysis is carried out in solutions containing not more than 1 per cent. of saccharides. The factor of reversion must be taken into account and conditions (concentrations) suitably adjusted in qual. and quant. determinations of saccharide components in acid food-products, processed in conditions of heat. S.C.I. ABSTR.

446. **The determination of trichloroethylene in air by the Rayleigh interferometer.** R. E. Jahn (British Oxygen Co. Ltd., Deer Park Road, London) (*Analyst*, 1955, **80**, 700–704).—The use of the Rayleigh gas interferometer as a convenient routine method for the determination of 0 to 3 per cent. of trichloroethylene vapour in air is described, the difference of refractive index between air and the unknown mixture being measured. Four methods of calibrating the instrument for this purpose are described. A. O. JONES

447. **Identification of substituted aliphatic amines.** T. Eckert (*Dtsch. ApothZtg*, 1955, **95** [27], 646–647).—A method is described by which secondary and tertiary N-alkyl-substituted aliphatic amines are identified by a colour reaction. A few mg of the free base are heated at 200° C for 10 min., cooled and treated with 5 drops of a 10 per cent. *p*-dimethylaminobenzaldehyde soln. in methanol. Subsequent dropwise acidification with dil. HCl produces a deep magenta coloration. A preliminary cold test is recommended to ensure that no other colour-producing components are present (as in procaine). The method has been successfully applied to a number of amines (dibucaine hydrochloride, mepacrine hydrochloride, triethanolamine, dibutylamine, etc.). Its specificity is demonstrated by a positive reaction with diethylaminoethylbenzhydryl ether and a negative result with the corresponding dimethyl compound, a positive reaction with ω-butylamino-6-chloro-2-methylpropionanilide and a negative result with the corresponding acetanilide. S.C.I. ABSTR.

448. **Hydroxamic acids. IV. Colorimetric microdetermination of oximes. "Oxime number."** E. E. Vonesch and O. A. Guagnini (*An. Asoc. Quím. Argent.*, 1955, **43** [1], 62–66).—A 0·01 to 0·5 per cent. oxime solution (0·1 to 1·0 ml), 0·2 ml of 2 per cent. H_2SO_4 and 1 ml of H_2O are heated on the water bath for 15 to 20 min. (this is sufficient time for even dimethylglyoxime to be hydrolysed). The solution is cooled, treated with 0·5 ml of 4 per cent. formaldehyde and 2·5 ml of 1 per cent. ferric alum and made up to 10 ml with water. Finally, 50 to 100 mg of $(NH_4)_2S_2O_8$ are added and, after 10 min., the colour is determined at 515 mμ. The sensitivity is $\simeq$ 0·1 μg (1 in 50,000) and the accuracy is better than 1 per cent. for 200 to 4000 μg. Furfuraldehyde, vanillin, salicyl- and cinnamaldehydes interfere. The "oxime number" is defined as the quantity of hydroxylamine in μg produced by 1 mg of the sample. T. P. MCLAUGHLIN

449. **New volumetric methods in the analysis of organic substances. I. Determination of allyl *iso*thiocyanate.** A. Berka and J. Zýka (Karlovy Univ., Prague, Czechoslovakia) (*Českosl. Farmac.*, 1955, **4** [5], 222–225).—The present methods of analysis and their drawbacks are discussed. A more convenient and rapid method was developed, based on the conversion of allyl *iso*thiocyanate into allylthiourea by boiling with aq. NH_3. The allylthiourea is then titrated with a standard solution of an oxidising agent, a potentiometric method being

used for end-point determination. Details of the titration with KIO_3 and $KBrO_3$ are given. The iodate titration is carried out in *N* HCl; the end-point is taken as the first inflection (occurring at $\simeq$ 120 mV) of the initially steady value of the potential. The same applies to the bromate titration, but here the medium is 7 *N* HCl at 90° C, to which a small amount of KBr is added. The inflection occurs at $\simeq$ 90 mV. In both cases an electronic voltmeter is used, the indicating electrodes being platinum wires and the comparing electrode the S.C.E. The procedures for determining allyl-*iso*thiocyanate in the oil, seed and alcoholic extract of mustard are also given. The method can also be applied to the determination of thiourea.

A. O. JAKUBOVIC

450. **Detection of phenols in bitumen by two-dimensional paper-chromatography.** M. R. Verma and R. Dass (Nat. Phys. Lab. India, New Delhi) (*Bitumen, Teere, Asphalte, Peche*, 1955, **6** [8], 253–257).—A method of detecting phenol and *o*-, *m*- and *p*-cresols separately in bitumens is described. Approximately 0·01 ml of a 10 per cent. solution of the bitumen in benzene is applied to a corner of a No. 1 Whatman paper (previously sprayed with 1 per cent. Na_2CO_3 soln.), and developed with ethanol. The paper is then dried, pressed against paper impregnated with diazotised sulphanilic acid, and redried. The bitumen spot is cut out, and the paper is developed at right angles with ethyl methyl ketone. Phenol and the individual cresols give characteristic coloured bands, and can be distinguished when present in the bitumen at a concn. of 0·1 per cent. A. B. DENSHAM

451. **The analysis of mixtures of phenols by partition chromatography and ultra-violet spectrophotometry.** R. M. Pearson (Imperial Chemical Industries Ltd., Billingham Division, Billingham, Co. Durham, England) (*Analyst*, 1955, **80**, 656–664).—A method is described for the determination of mixtures of phenol, cresols, xylenols and ethylphenols. These are separated by partition chromatography into groups which can be analysed spectrophotometrically. Two lengths of column of silica gel are used, *viz*, a 500-mm length (diam. 18 mm) with water as the stationary phase being suitable for mixtures of phenols and cresols only, and a 900-mm column with 30 per cent. aq. 2-methoxyethanol as the stationary phase being used when xylenols or ethylphenols, or both, are also present. The sample is dissolved in *cyclo*hexane and applied to the column in an apparatus with a specially designed reservoir and provision for application of pressure. Elution is continued with *cyclo*hexane, and 5-ml fractions are collected. Optical densities are measured at 270 to 284 mμ. The location of the absorption peaks and the extinction coefficients of each phenol should be determined for the particular spectrophotometer used. Examples are given of the calculation of results for single-component fractions and multiple-component mixtures. The determination of phenol can be made within an accuracy of 0·5 per cent. of the amount present. The accuracy of the cresol determination is within $\simeq$ 1 per cent. A. O. JONES

452. **Separation of coumarin and its derivatives by paper chromatography.** S. Berlingozzi and L. Fabrini (Univ. Florence, Italy) (*Sperimentale*, 1954, **5** [1–2], 1–5).—Good separation of mixtures containing three or four of the following compounds is claimed: coumarin, 7-methylcoumarin, umbelliferone, 4-methylumbelliferone, herniarin, daphnetin, diphenylumbelliferone and aesculetin in quantities of 1 to 10 μg. The method comprises the ascending chromatography of alcoholic solutions on Whatman No. 1 strips (55 cm long and 7 to 12 cm wide, according to the number of compounds to be separated). Elution is by an H_2O - acetic acid - butane-1:3-diol mixture (86:10:6). Spots are directly identified by fluorescence in Wood's light. The R_F coefficients for the substances under examination are given, and several chromatograms are reproduced. H. A. FISHER

453. **High-frequency titrimetry: the titration of organic bases, phenols and enols.** E. S. Lane (Atomic Energy Research Estab., Harwell, nr. Didcot, Berks., England) (*Analyst*, 1955, **80**, 675–681).—The apparatus used for high-frequency titrimetry in non-aqueous solvents is that of Dowdall *et al.* (*Anal. Abstr.*, 1955, **2**, 3552), and a procedure is described for the determination of the equiv. wt. of selected classes of organic compounds, including bases, quaternary ammonium salts and organophosphorus compounds. The general method of use is that previously described (*loc. cit.*). Examples of the application of the apparatus to the determination of equiv. wt. by titration with $HClO_4$ in glacial acetic acid and ethylenediamine are given. Results obtained by the method are quoted and discussed. A. O. JONES

454. **Detection of chloranil in spot analysis.** F. Feigl, V. Gentil and J. E. R. Marins (Min. Agric. Lab., Rio de Janeiro, Brazil) (*Anal. Chim. Acta*, 1955, **13** [3], 210–213).—As little as 0·25 μg of chloranil (tetrachloro-*p*-benzoquinone) can be selectively identified by mixing the sample with a 1 per cent. solution of tetramethyldiaminodiphenylmethane in ether and then slowly evaporating the ether; a blue diphenylmethane dye indicates the presence of chloranil. The sensitivity of the test is 1 in 250,000. A spot test for the analysis of aromatic compounds consists in heating the sample with $KClO_3$ and conc. HCl and then identifying chloranil, if formed, by the above-mentioned reaction. Tests on 71 such compounds show that, with typical exceptions, they are converted into chloranil. W. J. BAKER

455. **Determination of pyridine by use of the reaction with copper and thiocyanate.** Soichirô Musha and Makoto Munemori (*J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** [5], 393–396).—Experimental conditions for the determination of pyridine ($\simeq$ 0·1 g) by the use of the precipitation reaction with Cu^{++} and SCN' were studied. The pptn. of $Cu(C_6H_5N)_2(SCN)_2$ is complete at pH 5·2 to 5·7. The sample is treated with a small excess of 0·1 *M* $Cu(NO_3)_2$ and a known excess of 0·1 *M* KSCN soln. (25 to 50 ml) in a 100-ml calibrated flask and the pH is adjusted. The soln. is made up to 100 ml, filtered through dry paper and a 50-ml portion is made acid with 6 *N* HNO_3 (5 ml). The product is treated with 0·1 *N* $AgNO_3$ (25 ml) and the excess of Ag is titrated with standard KSCN soln. K. SAITO

456. **Chemical analysis of pyridine homologues by the use of ultra-violet absorption spectra.** Eiiti Tsunetomi (*J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** [2], 130–132).—The spectrochemical analysis of pyridine, 2:6-lutidine, and α-, β- and γ-picolines in admixture was studied in 0·1 *N* H_2SO_4. By the use of two neighbouring key bands for one

component (Vaughn *et al.*, *Brit. Abstr. C*, 1950, 277) (*e.g.*, 257 and 265 mμ for pyridine, 270 and 276 mμ for α-picoline, and 280 and 288 mμ for 2:6-lutidine), the composition can be determined with an error of $< \pm 1$ per cent. The optical densities are in accord with Beer's law for values up to 0·8. The sample is dissolved in 0·1 *N* H_2SO_4 (0·05 g per 25 ml) and weighed. A 0·125-g portion of this soln. is diluted with 0·1 *N* H_2SO_4 (25 ml) and submitted to measurement. A similar method can be applied to the analysis of a small amount (up to 3 per cent.) of α-picoline in pure pyridine, 2:6-lutidine and γ-picoline in pure β-picoline, and β-picoline and 2:6-lutidine in γ-picoline. K. SAITO

457. **Analysis of quinoline and *iso*quinoline fractions by the use of infra-red absorption spectra.** H. Kamada, S. Tanaka and K. Arakawa (*Japan Analyst*, 1954, **3** [5], 399–403).—The i.r. spectra of quinoline (max. absorption 12·47 μ), *iso*quinoline (12·15 μ), 2-methylquinoline (12·28, 13·42 μ) and 8-methylquinoline (12·24, 12·68 μ) were observed in CS_2 soln., and their use in industrial analysis was studied. The quinoline fraction of coal tar can be regarded as a binary mixture of quinoline and *iso*quinoline, since the absorptions of the methylquinolines are very faint. The two components are analysed by measuring the extinctions at 12·15 and 12·47 μ; these are in accord with Beer's law for up to 15 mg per ml of the CS_2 soln. The *iso*quinoline fraction contains significant amounts of 2- and 8-methylquinolines besides quinoline and *iso*quinoline and is analysed by the use of four key bands—12·15, 12·47, 12·68 and 13·42 μ. When the content of methylquinolines is low, it is advantageous to put the soln. of quinoline and *iso*quinoline into the compensating optical path. The average deviation from the mean is 0·7 per cent. for 2-methylquinoline and 0·6 per cent. for 8-methylquinoline. The *iso*quinoline fraction generally contains a significant amount of quinaldine, but its presence does not interfere with the analysis of other components. K. SAITO

458. **The determination of benzene in cracked hydrocarbons.** T. R. Crompton and V. W. Reid (Petrochemicals Ltd., Urmston, Manchester, England) (*Analyst*, 1955, **80**, 605–607).—A method has been developed for the determination of benzene in the lower-boiling unsaturated hydrocarbons produced by commercial cracking processes. These hydrocarbons, particularly the diolefins, absorb very strongly in the u.v. region used for the spectrophotometric determination of benzene. Olefins and diolefins are therefore rendered non-volatile by heating the sample under reflux with a mixture of activated clay and maleic anhydride, with *iso*octane as the reaction medium. Benzene is then separated from the mixture by distillation, and is determined spectrophotometrically at the selected wavelengths 252·5, 254·7 and 259·0 mμ. The accuracy of the method is shown to be $\simeq \pm 2$ per cent. of the determined benzene content. A. O. JONES

459. **Chromatographic procedures for the separation of water-soluble acid dye mixtures.** R. N. Sclar and K. A. Freeman (Food and Drug Admin., Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [3], 796–809).—When a paper-chromatographic separation procedure, employing aqueous 2-methoxyethyl acetate, is applied to a mixture of the 14 (U.S.A.) permitted water-soluble coal-tar food dyes, 10 coloured zones (not necessarily separated) are observed, and the dyes present in a mixture can therefore be tentatively identified. A method of general column chromatography, with powdered cellulose, for the separation of dyes for spectrophotometric analysis is given, together with a scheme for the systematic separation of the 14 dyes which are adsorbed on a column from 20 per cent. NaCl soln. and then eluted with various solvents and further separated on other cellulose columns. A. A. ELDRIDGE

460. **Chemical method for the determination of protein rayons in mixtures with wool.** E. Druce (*J. Text. Inst. Manchr Trans.*, 1955, **46** [7], 512–520).—See *Anal. Abstr.*, 1955, **2**, 2144.

461. **The qualitative analysis of surface-active agents.** V. W. Reid, T. Alston and B. W. Young (Petrochemicals Ltd., Urmston, Manchester) (*Analyst*, 1955, **80**, 682–689).—A simple qualitative scheme for the identification of surface-active agents is described, the necessity for a large number of chemical tests being reduced by spectrophotometric examination. The active agent is separated from fillers, etc., by the methods of Gilby *et al.* (*Mfg Chem.*, 1950, **21**, Nos. 9 and 10), the dried residue being extracted with ethanol and the insol. inorganic matter removed by filtration. The dried separated active ingredient is dissolved in water ($\simeq$ 5 g per litre), any turbidity being removed by addition of ethanol. The soln. is diluted suitably for spectrophotometric examination and the spectrogram (210 to 350 mμ) is compared with those of reference compounds. Tests for ionic character and for the presence of N assign the compounds to four main groups, and each group is subdivided according to the characteristics of the spectrogram. By this means an unknown active agent is assigned to its class and further chemical tests can then be made. Eighteen examples are given of the absorption graphs obtained, and their similarity to those of the reference compounds is exhibited. A. O. JONES

462. **Partition chromatography of synthetic detergents.** F. Franks (British Launderers' Res. Ass., Hendon, London) (*Nature*, 1955, **176**, 693–694).—Ascending and circular chromatography were employed for separating mixtures of synthetic detergents, mainly normal sodium alkyl sulphates with hydrocarbon chains containing 12 to 18 carbon atoms. With minor modifications the method was successfully applied to alkylaryl-sulphonates, secondary alkyl sulphates, quaternary ammonium and pyridinium salts. Whatman No. 1 filter-paper was impregnated with a long-chain fatty alcohol, usually cetyl alcohol, which acted as stationary phase; this was applied from a 1 per cent. ethanolic solution. The mobile phase consisted of aqueous ethanol saturated with cetyl alcohol, the concentration varying according to the alkyl sulphates to be separated. The chromatogram was developed for 10 to 24 hr., the paper was dried, then immersed in 0·5 per cent. cupric acetate and sprayed with a 0·05 per cent. solution of rhodamine 6GB. After being dried, the detergent spots appeared crimson on a pink background in daylight, and dark purple on a yellow background under u.v. light. The R_F values determined for various concentrations of ethanol are tabulated. By a similar procedure "Teepol" was resolved into six well-defined components and commercial cetylpyridinium chloride into four distinct compounds. O. M. WHITTON

463. **The rapid determination of total fatty acid in unbuilt soap products.** H. L. Webster and A. Robertson (Thos. Hedley & Co., Newcastle upon Tyne) (*Analyst*, 1955, **80**, 616–619).—A method is described for the determination of total fatty acid in unbuilt soaps, *i.e.*, soaps to which no extraneous materials have been added to improve their effectiveness under the conditions of use. The sample is dissolved in warm water and the soln. is treated with a measured excess of standard $CaCl_2$ soln. and brought just to boiling point. The calcium soaps are removed by filtration, the filtrate is treated with NaOH soln. and the excess of Ca is determined by titration with 0·1 *M* EDTA (disodium salt) in the presence of murexide as indicator. A correction is required for small amounts of Na_2CO_3, if present. The method is carried out in 15 min. With modifications it is applicable to built soaps, but then has little advantage over the conventional method.

A. O. JONES

464. **Analysis of lipsticks.** J. E. Clements (Food and Drug Admin., Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [3], 838–843).—The residue after treatment of the lipstick with trichloroethylene and acetone consists of lakes and fillers; the extract, after removal of solvent, when dissolved in heptane and extracted with 95 per cent. acetic acid affords (*a*) in the heptane fraction, hydrocarbons and waxes, which are separated chromatographically on alumina, and (*b*) in the acetic acid fraction, ricinoleic esters and dyes. From the latter fraction, after dilution and extraction with ether, fluorescein dyes are obtained by extracting the ether fraction with 3 per cent. KOH; ricinoleic esters remain in the ether fraction. Propane-1:2-diol is determined by dissolving the lipstick in heptane, adding water, distilling, and employing Malaprade's reaction (*Bull. Soc. Chim.*, 1934, [V], **1**, 833).

A. A. ELDRIDGE

465. **Polarographic determination of autoxidation products in methacrylates.** M. Bohdanecký and J. Exner (Výzkumný ústav synthetických pryskyřic, Pardubice, Czechoslovakia) (*Chem. Listy*, 1954, **48** [10], 1506–1510).—Peroxides and pyruvates, the autoxidation products of methacrylates, can be determined polarographically in a medium of a mixture (1 + 1) of benzene and methanol, with 0·3 *M* LiCl as basic electrolyte. The accuracy of the method is ± 2 per cent. for peroxides and ± 5 per cent. for pyruvates; the minimum amounts determinable are 0·04 millimole of peroxidic oxygen and 0·001 per cent. of pyruvate per litre of methacrylate.

G. GLASER

466. **Mass-spectrometric determination of methacrylic acid in methyl methacrylate.** Shun Araki and Yuji Takayama (*J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58** [1], 15–17).—The mass-spectrometric determination of methacrylic acid (**I**) (< 1 per cent.) in monomeric methyl methacrylate (**II**) was studied by the use of the peak *M/e* 86, where *M/e* is the ratio of mol. wt. to charge. The "background" at the peak *M/e* 86 is calibrated by the measurement of the peak of **II** *M/e* 82. **I** is readily adsorbed on the surface of the vessel; attempts were made to eliminate this effect, but it was found that an empirical calibration factor must be used for the determination of a small amount of **I**. The height of the peak *M/e* 86 increases slightly with time; the value must be measured immediately after the initiation of the flow. No interference results from the presence of methyl α-hydroxy*iso*butyrate.

K. SAITO

467. **Analytical investigations on synthetic drying oils.** K. Wekua and J. Bergmann (*Farbe u. Lack*, 1955, **61**, 324–330).—The analysis of synthetic drying oils, prepared by the chlorination and dechlorination (with Zn in dioxan) of tristearin, triglycerides of synthetic fatty acids, olive oil, etc., in particular the determination of the degree or type of unsaturation, has been studied. The normal iodine-value methods gave widely divergent results, varying from 83 by the Wijs method to 180 by the Woburn method for a typical oil, compared with 285 estimated from the Cl removed on dechlorination. Unsaturation could not be determined by hydrogenation in acetic acid solution with Pt, as reaction was very slow, but most of the oils could be hydrogenated in dioxan solution with Pt, the hydrogen iodine value of the above oil being 250. The wide divergence of iodine values indicated the presence of some conjugated unsaturation. This was confirmed by u.v. spectra, but quant. determination was not possible owing to high general absorption, possibly arising from interference by residual Cl in the oils (≃ 12 per cent.), carboxyl groups, side-chains, etc. Diene values could be determined by the interaction of the oil with maleic anhydride in toluene, and ranged from ≃ 20 to 30; these could be considered min. values for the conjugation.

L. A. O'NEILL

468. **Constitution of lac. I. Reactivity of lac resin.** H. A. Bhatt, N. R. Kamath and J. M. Nadkarni (*J. Sci. Ind. Res., B, India*, 1955, **14** [6], 270–275).—Previous work on the reactivity of lac resin is reviewed. It was apparent that certain reactions peculiar to lac resin could not be explained only on the basis of the free and combined hydroxyl and carboxyl groups. Tests were carried out to determine whether a carbonyl group was present, which would account for these reactions. All the usual grades of lac gave definite carbonyl values when examined by the hydroxylamine hydrochloride, sodium sulphite, and alkaline hydrogen peroxide methods. The presence of an aldehyde group in the lac resin has been confirmed. A recommended method for the estimation of the carbonyl value of lac, based on the sodium sulphite method, has been developed and is described. *Procedure*—Lac (0·5 g) is dissolved in 20 ml of alcohol, cooled, and titrated against 0·1 *N* NaOH to a permanent bluish green. Thymolphthalein is used as indicator for all titrations. A blank is carried out with all the reagents except lac. The acid value is then calculated from the equation given. To determine the carbonyl value, 0·5 g of lac is dissolved in 20 ml of alcohol and cooled. To the lac soln. are added 5 ml of water and 20 ml of Na_2SO_3 soln.; the soln. is shaken, then set aside for 5 min., and the residual acidity is determined by titrating with 0·1 *N* NaOH. A blank is run with all the reagents except lac to determine the free alkalinity of aq. alcohol containing Na_2SO_3 soln. by titrating with 0·1 *N* HCl. The carbonyl value is then calculated from the equation given.

G. C. JONES

469. **Flash-point determination of varnishes.** W. Heilmann (*Farbe u. Lack*, 1955, **61**, 330).—Errors occur in the determination of the flash point of viscous varnishes by the Abel - Pensky apparatus owing to slow heat transfer. Modifications involving the introduction of either a stirrer, or thermocouples to record the overall temp. of the varnish, are suggested.

L. A. O'NEILL

470. **Determination of sulphur content in rubber vulcanisates by high-frequency titration.** I. Yamaji (*Rep. Tokyo Chem. Ind. Res. Inst.*, 1955, **50** [6], 203–206).—Free S in rubber vulcanisates was determined by oxidising the acetone extract to sulphate, dilution, neutralisation and adjustment of the solution to contain 35 to 45 per cent. of ethanol, followed by high-frequency titration with 0·05 *N* or 0·2 *N* $BaCl_2$ solution. To determine total S, the solution was passed through a column of cation-exchange resin to prevent the interference of other cations formed by the destructive oxidation of vulcanisates. The method is accurate and more rapid than gravimetric methods. S.C.I. Abstr.

See also Abstracts 532, 537, 592, 603, 624.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

471. **Stability of alkaline solutions of haematin.** J. F. Scaife (Dominion Lab., D.S.I.R., Wellington, N. Zealand) (*Analyst*, 1955, **80**, 562–565).—The method for determining haemoglobin and myoglobin by conversion into alkaline haematin is critically examined and the investigation has revealed some of the conditions affecting the behaviour of alkaline haematin. The normal alkaline-haematin method (Clegg *et al.*, *Brit. Med. J.*, 1942, **2**, 329) has been modified to make it suitable as a comparative method of analysis for either blood haemoglobin or tissue myoglobin. The determination is made spectrophotometrically at 380 mμ; at this wavelength, results are reliable and reproducible. Standard solutions of haemin in alkali are not stable, but show progressive fading, which is accelerated by exposure of the soln. to light or heat, by agitation with air, or by the presence of traces of Cu.

A. O. Jones

472. **Micro-determination of sulphur in biological material.** J. Broekhuysen and J. Béchet (Inst. Emile Gryson, Brussels, Belgium) (*Anal. Chim. Acta*, 1955, **13** [3], 277–280).—By ignition of the sample in an oxygen bomb and boiling the leached products with H_2O_2 all the sulphur is oxidised to sulphate, which is then pptd. with 0·004 *M* $BaCl_2$ in boiling HCl, complete pptn. being ensured by finally raising the pH to ≃ 3·5 with aq. NH_3. A vol. of 0·004 *M* aq. K_2CrO_4 equiv. to that of the $BaCl_2$ introduced initially is added, plus two drops of 10 per cent. aq. $AlCl_3$, and the excess of $BaCl_2$ is co-pptd. (as $BaCrO_4$) with the colloidal $Al(OH)_3$ at pH 9 (aq. NH_3) in the presence of ethanol. The excess of K_2CrO_4 is then determined colorimetrically at 370 mμ. From 1 to 5 mg of S in each sample can thus be determined, although a slight modification lowers this limit to 0·1 mg. The accuracy is within 2 to 3 per cent. W. J. Baker

473. **A method for the estimation of hydrogen sulphide in biological material.** O. Karges and K. Lang (Johannes Gutenberg Univ., Mainz, Germany) (*Klin. Wochschr.*, 1955, **33** [33–34], 825).—By using a specially designed apparatus H_2S is determined by the diffusion technique. A beaker which acts as the absorption vessel is fitted with a ground-glass stopper carrying a gas-delivery tube, the end of which is turned up to form a container for the reaction fluids, and a dropping funnel directed so that it delivers into the reaction vessel. The absorption liquid (Zn acetate 50 g, Na acetate 10 g, NaCl 0·05 g, water to 1000 ml) is placed in the beaker and the test liquid in the reaction vessel; the apparatus is closed, air is displaced by nitrogen and the H_2S is liberated by running in 40 per cent. H_3PO_4. After 3 hr. the absorbed H_2S is determined by the methylene blue reaction.

H. F. W. Kirkpatrick

474. **Iron estimation in serum with *o*-phenanthroline.** F. Scheibl and D. Saffer (Med. Chem. Inst., Univ. Innsbruck, Austria) (*Hoppe-Seyl. Z.*, 1954, **298** [6], 272–277).—The pH, the concentration of *o*-phenanthroline and the time at which the reagents are added are important. Optimal conditions were studied and a method satisfactory for amounts from 0·2 to 5 μg of iron is proposed. *Procedure*—Mix the serum (2 ml) and HCl (1 + 1) (1 ml) thoroughly and set aside for 10 min. Deproteinise with 20 per cent. trichloroacetic acid (2 ml) and filter after a further 10 min. To the filtrate (2·5 ml) add a drop of *p*-nitrophenol soln. and then 0·5 per cent. aq. NH_3 until the soln. is yellow. Exactly neutralise with 0·2 *N* H_2SO_4 and then add an excess of 0·6 ml of H_2SO_4 and, after mixing well, set aside for 30 min. Add 2 per cent. quinol (0·5 ml) and 0·5 per cent. *o*-phenanthroline (0·5 ml) and make up to 7 ml with twice-distilled water. Measure the extinction at 510 mμ after ⩽ 10 min. The colour does not alter if the soln. is allowed to stand longer. A blank is prepared simultaneously, 2 ml of twice-distilled water being used in place of serum. F. Powell

475. **A simple procedure for the study of ionic regulation in small animals.** J. Shaw (King's Coll., Newcastle upon Tyne, England) (*J. Exp. Biol.*, 1955, **32** [2], 321–329).—The micro-methods described are suitable for determining 1-μg amounts of Ca, Mg, K and Na in small vol. of body fluids. Calcium is pptd. as oxalate, Mg with 8-hydroxyquinoline after removal of Ca, K as chloroplatinate and Na with zinc uranyl acetate. By suitable treatment of the separated ppt. in each case, Cl′ is obtained in an amount equivalent to the metal to be determined. The Cl′ is then titrated with standard $AgNO_3$ by Volhard's method or electrometrically, a simple micro-burette being used. The standard deviation of the assay for Na is 2 to 4 per cent. and for the remaining elements 1 to 2 per cent.

W. H. C. Shaw

476. **Determination of glucose in biological material by a compleximetric method.** H. Bultasová and E. Horáková (Biochem. Lab., Thomayerova Nemocnice, Prague, Czechoslovakia) (*Chem. Listy*, 1954, **48** [11], 1698–1700).—The method is based on the reduction of alkaline $CuSO_4$ and the determination of the separated Cu_2O, dissolved in HNO_3, by compleximetric titration with EDTA to murexide as indicator. To determine glucose in cerebrospinal fluid, heat the sample (0·5 ml) with the reagent [prepared by dissolving tartaric acid (7·5 g) and $CuSO_4.5H_2O$ (4·5 g) in a soln. of anhyd. Na_2CO_3 (40 g) in water (100 ml) and diluting to 1 litre] (3 ml) in a bath of boiling water for 20 min., cool and centrifuge. Wash the ppt. of Cu_2O twice with H_2O (2 ml) by centrifuging and decanting, dissolve it in warm 10 per cent. HNO_3 (0·3 ml), cool, add 2·5 per cent. aq. NH_3 (1 ml), H_2O (9 ml) and the indicator, and titrate with 0·01 *M* EDTA (disodium salt) until the colour changes from yellow to violet. Glucose in blood and urine is determined

similarly, but in each instance the material must be first deproteinised by treatment with 10 per cent. Na_2WO_4 and 0·66 *N* H_2SO_4. G. GLASER

477. **Colorimetric determination of pyruvic acid and other α-keto acids in sub-microgram quantities.** S. L. Bonting (Colley Med. State Univ., Iowa City, U.S.A.) (*Arch. Biochem. Biophys.*, 1955 **58** [1], 100–108).—The method given by Friedeman and Haugen (*J. Biol. Chem.*, 1943, **147**, 415) is adapted for the determination of 0·1 to 1·0 μg of pyruvic acid or other α-keto acids in samples containing at least 2 μg of these acids per ml. Increased colour stability and sensitivity and lower blanks are obtained by reading the aq. Na_2CO_3 extract at 380 mμ, omitting the addition of NaOH. Separate deproteinisation of the sample is found unnecessary and details are given for the differential determination of pyruvic acid and either α-oxoglutaric or oxalacetic acid. W. H. C. SHAW

478. **Micro-analysis of glucuronide glucuronic acid as applied to β-glucuronidase and glucuronic acid studies.** W. H. Fishman and S. Green (Cancer Res. Lab., New England Center Hosp., Boston, Mass., U.S.A.) (*J. Biol. Chem.*, 1955, **215** [2], 527–537).—A sensitive method is described for the determination of glucuronides in the presence of glucuronic acid. It is based on prior oxidation of the glucuronic acid and other interfering aldehydic substances with hypoiodite at pH 10·1, and the unaffected glucuronide is then determined by the 1:3-dihydroxynaphthalene colour reaction (Tollens and Rorive, *Ber. dtsch. chem. Ges.*, 1908, **41**, 1783; Mandel and Neuberg, *Biochem. Z.*, 1908, **13**, 148). Under the strongly acid conditions of this test, the glucuronide is hydrolysed to the free acid, which gives a violet product with the reagent, and the intensity of the colour is measured photocolorimetrically. The amount of free acid can be ascertained by a determination before and after oxidation, but this method is valid only in the absence of interfering amounts of hexoses. The sensitivity of the method is 2 μg of glucuronide glucuronic acid and the standard deviation is $\simeq \pm$ 3 per cent. The method can also be used for the determination of β-glucuronidase activity; phenolphthalein glucuronide is used as substrate, and determination of the liberated glucuronic acid is more specific than the determination of the increase in reducing power. J. N. ASHLEY

479. **Colorimetric and spectrophotometric determination of 5-hydroxyindol-3-ylacetic acid (5-HIAA).** P. Correale (*Experientia*, 1955, **11** [8], 315–316.)—Colorimetric and spectrophotometric methods may be employed in the quant. determination of 5-HIAA in pure soln. or aq. eluates of 5-HIAA spots from paper chromatograms. They cannot be applied directly to biological fluids or crude extracts of biological materials, because of interfering substances present. The colorimetric method is based on the *p*-dimethylaminobenzaldehyde reaction. One vol. of a freshly prepared 2 per cent. soln. of this reagent in conc. HCl is added to 2 vol. of the liquid under investigation. The tubes are then placed in a water bath at 56° to 58° C for 10 to 12 hr. The coloured soln. are read within 3 hr. in a Beckman spectrophotometer at 600 mμ. Beer and Lambert's law is valid between 2 and 25 μg of 5-HIAA per ml. For the u.v. absorption spectrum method aq. soln. of 5-HIAA are adjusted to pH 7·0 and in u.v. light show a max. absorption at 221 mμ. Beer and Lambert's law is valid between 1 and 15 μg of 5-HIAA per ml. On eluates of urine chromatograms, satisfactory results were obtained with only the colorimetric method and only for intense and pure 5-HIAA spots. R. S. TONKS

480. **The separation of direct and indirect bilirubin by paper chromatography.** G. Gries, P. Gedigk and J. Georgi (Med. Klin. und Path. Inst., Univ. Marburg, Germany) (*Hoppe-Seyl. Z.*, 1954, **298** [3–5], 132–139).—Ascending chromatograms were run in glass cylinders protected from light with black paper, in an atmosphere of nitrogen and with alkaline pyrogallol in the bottom of the vessel. As developing solvents, various buffers or chloroform were used. In acid or neutral soln. indirect bilirubin does not travel. Direct bilirubin travels with essentially the same R_F value from pH 2 to 12. Indirect bilirubin first begins to move at pH 7 to 9, the R_F value increasing rapidly with increase in pH. When both pigments are applied at the same spot, an alteration in the R_F value of the indirect bilirubin is frequently observed. No alteration in the proportion of the pigments is ever observed. When the diazo reaction is applied in an acid medium on paper, both forms of bilirubin react immediately, so the velocity of reaction cannot be used as a means of distinguishing one form from the other. The spots may be eluted with 0·1 *N* NaOH. Indirect bilirubin in protein-free solution is oxidised more readily than direct bilirubin and is therefore subject to greater losses on elution. The disodium salt of indirect bilirubin is sol. in water and not in chloroform and behaves as direct bilirubin on being chromatographed. F. POWELL

481. **Detection of a series of different urinary indicans and indicanoids, and similar metabolic products of skatole and 2-methylindole, by means of a new paper-chromatographic indican reaction, the fluorindal reaction.** P. Decker (Lab. der II med. Klin. der Univ. Munich, Germany) *Hoppe-Seyl. Z.*, 1955, **300** [5–6], 245–251).—The application of heat with the addition of Ehrlich's aldehyde reagent (**I**) reveals some but not all indicans. The coloured product formed from **I** and indoxylsulphuric acid is yellow in non-polar and red in polar solvents. The sensitivity of **I** on paper chromatograms can be greatly increased by subsequent spraying with aq. NH_3 and examining in u.v. light. The appearance of a fluorescence under these conditions is termed the fluorindal reaction and is obtained only on paper. By means of this reaction not only indoxylsulphuric acid and indoxylglucuronic acid, but at least four other substances, which can be distinguished by their R_F values, may be detected in normal and pathological human urine and in the urine of dogs fed with indole. Related substances termed skatole indicanoids can be detected in the urine of dogs fed with skatole. A similar substance is found after feeding with 2-methylindole. The indicans and indicanoids can also be separated by column chromatography on carbon - kieselguhr. Their possible constitution is discussed and absorption spectra are given. F. POWELL

482. **A method for the estimation of fatty acid esters.** M. H. Hack (Tulane Univ., New Orleans, La., U.S.A.) (*Arch. Biochem. Biophys.*, 1955, **58** [1], 19–23).—The method described is based on the formation of a lavender colour when the hydroxamic acids produced by treating fatty acid esters with alkaline NH_2OH are treated with $Fe(ClO_4)_3$. *Reagents*—(*i*) 0·625 *M* NaOH in ethanol saturated

with Na_2CO_3. Filter. (*ii*) 0·36 *M* $NH_2OH.HCl$ in ethanol. (*iii*) Dissolve 2 g of $Fe(ClO_4)_3.6H_2O$ in 10 ml of water and 20 ml of 71 per cent. $HClO_4$. Allow to stand for 1 hr. (*iv*) Dilute 1 vol. of (*iii*) to 20 vol. with ethanol when required for use. *Procedure*—Evaporate in a stream of N an aliquot of lipid extract containing 0·2 to 3 μmoles of esters in a test-tube (17 mm × 150 mm) (calibrated at 10 ml) placed in a water bath at 60° C. Add 0·3 ml of (*ii*) and 0·4 ml of (*i*), mix and boil over a microburner for 15 sec. Cool for 5 min. and then wash down the sides of the tube with 1 ml of (*iv*). Mix and dilute to 10 ml with ethanol. Measure the colour after 30 min. at 520 mμ against a reagent blank. Calibration with methyl stearate is rectilinear with up to 3 μmoles of ester.

W. H. C. SHAW

483. **Application of the isotope derivative method to the analysis of pyrimidines.** J. R. Fresco and R. C. Warner (N.Y. Univ. Coll. Med., New York, N.Y., U.S.A.) (*J. Biol. Chem.*, 1955, **215** [2], 751–763).—A specific and sensitive method is described for the determination of microgram quantities of uracil and thymine. It is an isotope derivative method and depends on treatment of these pyrimidines with labelled *p*-iodobenzenesulphonyl ("pipsyl") chloride in 75 per cent. acetone, at room temp., buffered at pH 8·5 to 9·0 with tetramethylammonium bicarbonate. The resulting "pipsyl" derivatives are then determined by carrier or indicator procedures without the need for quant. isolation of these derivatives. "Pipsyl" chloride, labelled with ^{131}I and ^{35}S, is used in the carrier and indicator methods, respectively. J. N. ASHLEY

484. **The determination of amino acids.** B. Scheunemann (Univ. Leipzig, Germany) (*Pharm. Zentralh.*, 1955, **94** [4], 123–124).—The determination of ammonia nitrogen and amino-acid nitrogen in spices is carried out as follows. To 2·5 g of material add water (200 ml), a few drops of phenolphthalein solution, and freshly ignited MgO (2 g), and distil the NH_3 into 0·1 *N* acid (20 ml) for exactly 10 min. Back-titrate the excess of acid and calculate the ammonia nitrogen present. Cool the residue containing the amino acids, neutralise with HCl, filter, and make up to 250 ml. Transfer portions of exactly 50 ml into two Nessler tubes and to one add 10 ml of a solution of formaldehyde previously made just alkaline to phenolphthalein with 0·1 *N* alkali and mix. Titrate the now decolorised solution to the colour of the other solution with 0·1 *N* alkali, maintaining the volumes in the two tubes equal. Calculate the amino-acid nitrogen. P. S. STROSS

485. **A photometric method for the determination of proline.** W. Troll and J. Lindsley (May Inst. for Med. Res., Jewish Hosp. Ass., Cincinnati, Ohio, U.S.A.) (*J. Biol. Chem.*, 1955, **215** [2], 655–660).—A specific spectrophotometric method is described for the determination of proline in protein hydrolysates, urine and plasma. It is based on a modification of the method of Chinard (*Brit. Abstr. AIII*, 1953, 1250); the interfering basic amino acids, lysine, hydroxylysine and ornithine, are removed by shaking the soln. with Permutit. Hydroxyproline does not give the colour reaction with ninhydrin. *Procedure*—Shake the soln. (containing 1 to 5 × 10^{-5} *M* proline) with approx. 10 per cent. of its wt. of Permutit for 5 min. Heat the filtrate (5 ml) with acetic acid (5 ml) and the ninhydrin reagent (5 ml) [ninhydrin (125 mg), acetic acid (3 ml) and 6 *M* H_3PO_4 (2 ml); warm to 70° C to dissolve; the reagent is stable for at least 24 hr.] on a water bath for 1 hr. Cool, and shake with benzene (5 ml) for 5 min. Separate the benzene and determine the optical density spectrophotometrically at 515 mμ. Urine and plasma must be diluted at least 20- and 10-fold, respectively.

J. N. ASHLEY

486. **Polarographic determination of di-DNP-histidine. Determination of histidine.** P. E. Wenger, D. Monnier and S. Faraggi (Univ. of Geneva, Switzerland) (*Anal. Chim. Acta*, 1955, **13** [3], 293–299).—Between pH 8 and 10, at concn. of ≃ 12 mg per 100 ml, di(dinitrophenyl)histidine (**I**) (prepared as described) in a mixture (1:1) of basic buffer and water yields a polarogram having three steps. Maxima appear only at concn. > 1·0 mg per 10 ml and can be suppressed by adding four drops of aq. 0·2 per cent. poly(vinyl alcohol). Based on the use of two calibration curves, a polarographic procedure for the determination of **I** in amounts as low as 1 μg per ml is described. From 200 to 10 μg of histidine can be similarly determined by adding an excess of 1-fluoro-2:4-dinitrobenzene, in the presence of $NaHCO_3$, and removing the excess by a double extraction with ether. This excess, or the amount of **I** formed, can then be determined polarographically. The error varies from 0·5 to 10 per cent. according to concn. W. J. BAKER

487. **Use of turbidity curves for the quantitative determination of proteins in mixtures.** Z. Vodrážka (Ústav hematologie a krevní transfuse, Prague, Czechoslovakia) (*Chem. Listy*, 1954, **48** [11], 1684–1687).—Conditions have been studied under which the turbidity curves, obtained by the non-equilibrium pptn. of proteins, can be used for the determination of proteins in mixtures. The proteins should have the optimum concn. range of 10 to 30 mg per 25 ml. Picric acid, 0·05 *N* HCl or 1 per cent. aq. uranyl acetate have been used as pptg. agents. Picric acid is especially suitable for the analysis of blood plasma and serum.

G. GLASER

488. **The detection of adenine on paper chromatograms of nucleoprotein hydrolysates.** H. Boser (Forsch. Inst. für Diabetes, Griefswald, Germany) (*Hoppe-Seyl. Z.*, 1954, **298** [3–5], 145–150).—The purine or pyrimidine component of nucleotides can be detected on paper chromatograms by heating with 0·2 per cent. soln. of 1:2-naphthaquinone-4-sulphonic acid in half-satd. NaOH soln., when a deep-violet colour appears with adenine and a pure blue colour with guanine. The sugar component can be detected on another part of the chromatogram with aniline hydrogen oxalate. The reaction is of practical importance only for the detection of adenine in nucleoprotein hydrolysates. No amino acid gives a similar colour and, in nucleoprotein hydrolysates with 2 per cent. of organic P, the violet of adenine is the most marked colour of the whole chromatogram. Guanine is indistinguishable from the background of amino acids, but the reaction is useful for detecting guanine in protein-free hydrolysates of nucleic acid. The greenish-blue colour given by cytosine, which is only 0·01 as sensitive as the adenine colour, is too weak to be of use even in this respect; the colour given by thymine is also too weak. Acid mixtures for the development of chromatograms were found superior to alkaline ones in giving sharper spots and higher R_F values. F. POWELL

489. **Some new solvents for paper chromatography of phosphoric acid esters.** E. Gerlach, E. Weber and H. J. Döring (Pharmacol. Inst., Heidelberg Univ., Germany) (*Arch. exp. Path. Pharmak.*, 1955, **226** [1], 9–17).—Three different solvent mixtures composed of 3, 4 or 5 organic constituents in varying proportions are described; all contain formic acid and one contains trichloroacetic acid in addition. The mixtures are all suitable for the simultaneous separation of numerous phosphorus compounds, even from tissue extracts rich in ions; they can also be used for one-dimensional and two-dimensional ascending or descending chromatography and a saturated vapour atmosphere need not be maintained during their use. Details of the properties and methods of application of these mixtures are given, together with the advantages for their use with different types of compound. Three further mixtures of organic solvents containing NH_3 are given; the sharpness of the separation of nucleotides and phytic acid is greatly increased in the ammoniacal solvent by the addition of 8-hydroxyquinoline with or without EDTA (disodium salt). With four of the above-described solvents, the R_F values of 31 pure phosphorus compounds have been determined. P. HAAS

490. **The determination of oxidised and reduced diphosphopyridine nucleotide and triphosphopyridine nucleotide in animal tissues.** G. E. Glock and P. McLean (Courtauld Institute of Biochemistry, Middlesex Hospital, London) (*Biochem. J.*, 1955, **61** [3], 381–388).—Sensitive methods are described for the separate determination of diphosphopyridine nucleotide and triphosphopyridine nucleotide and of their reduced forms in animal tissues. These involve coupling the reduced co-enzymes (which are continuously formed in the presence of ethanol and alcohol dehydrogenase, or glucose-6-phosphate and its dehydrogenase, respectively) with their respective cytochrome-*c* reductases and determining the rate of reduction of cytochrome-*c* spectrophotometrically at 550 mμ. It is possible to determine the oxidised and reduced co-enzymes separately because of differences in their stability; the oxidised forms are relatively stable in dil. acid and the reduced forms in dil. alkali. Both solutions are neutralised before the determination. As little as 0·1 μg of co-enzyme can be accurately determined. J. N. ASHLEY

491. **A rapid method for estimation of total adrenal cholesterol.** A. C. Roy, S. N. Datta and R. N. Sur (*J. Sci. Ind. Res., C, India*, 1955, **14** [7], 124–125).—The method is based on the observation that a mixture of conc. H_2SO_4, glacial acetic acid and $FeCl_3$ solution forms a purple colour with serum cholesterol in acetic acid solution. The resulting colour obeys Beer's law and remains stable for several hours. The results compare favourably with those of the standard method. The method described may be utilised in the bio-assay of ACTH. G. C. JONES

492. **The effect of vitamin-A deficiency on the cholesterol levels of the plasma and liver of the rat. [Determination of cholesterol.]** B. Green, J. S. Lowe and R. A. Morton (Univ. Liverpool, England) (*Biochem. J.*, 1955, **61** [3], 447–453).—A modification of Kenny's method (*Biochem. J.*, 1952, **52**, 611) is described for the determination of cholesterol in small amounts of plasma. With 0·2 ml of plasma, or 0·15 to 0·2 mg of cholesterol, the results are reproducible to within ± 5 per cent. J. N. ASHLEY

493. **The colour reaction of phenolic steroids with perchloric acid.** D. Pontius (Endokrinol. Forschung. am Staatlichen Med. Untersuch., Trier, Germany) (*Hoppe-Seyl. Z.*, 1954, **298** [6], 268–271).—The Kober reaction has been improved by substituting $HClO_4$ for H_2SO_4 and adding picric acid. It has now been shown that salicylic acid can replace picric acid. *Procedure for urine.*—The residue from a purified benzene extract of 100 ml of urine is dissolved in 1 ml of chloroform, and 0·5 ml of freshly prepared $HClO_4$ reagent (0·1 ml of 70 per cent. acid in a mixture of 3 ml of peroxide-free ether and 7 ml of $CHCl_3$) and 1 ml of salicylic acid (50 mg per 100 ml of $CHCl_3$) are added. The soln. is heated for 5 min. in a bath of boiling water, evaporated to dryness and dissolved in chloroform - phenol mixture (4 ml of a mixture of 100 ml of molten phenol at 60° C and 250 ml of $CHCl_3$, cooled to room temp.). The soln. is divided into two parts—2 ml of soln. and 2 ml of peroxide-free ether for the test, and the remainder of the soln. and 2 ml of peroxide-containing ether for the blank. Readings are taken after 5 min., at 530 mμ. Quantitative recoveries were obtained when oestrone was added to the extract, but only 50 per cent. when added to hydrolysed urine. Similar recovery figures were obtained with the Zimmermann reaction. The reaction may be applied to the determination of other steroids. Dehydroisoandrosterone gives a blue colour and cholesterol a red. F. POWELL

494. **Studies on follicular hormone. VIII. Quantitative analysis of oestrone and oestradiol in pregnant-mare and stallion urine by paper chromatography, measuring the area of coloured spots.** Kakuma Nagasawa, Einosuke Koshimura and Seiichi Okazaki (Nat. Hyg. Lab., Tokyo) (*Pharm. Bull., Japan*, 1955, **3** [2], 144–147).—A 2 × 2-dose assay method was used for the quant. analysis of oestrone and oestradiol by chromatography on alumina-impregnated filter-paper by measuring the area of the spots obtained (*cf. Anal. Abstr.*, 1955, **2**, 425). Statistical analysis of the results shows the fiducial limits of error of the method to be smaller than those of bioassays. In fresh urine of pregnant mares, 2 per cent. of the oestrone present is free and 98 per cent. is conjugated, and 6 per cent. of the oestradiol is free and 94 per cent. is conjugated. About equal amounts of oestrone (39 μg per ml) and oestradiol (40 μg per ml) were found to be present in stored urine of stallions. P. S. STROSS

495. **A simple clinical chemical method for the determination of cholinesterase in serum.** R. Ammon and F. J. Zapp (*Klin. Wochschr.*, 1955, **33** [31–32], 759–762).—A new apparatus, simpler to construct and operate than the Warburg apparatus, is described for the manometric estimation of cholinesterase in serum. Details of its use, a definition of the units used and discussion of results obtained are given. H. F. W. KIRKPATRICK

496. **The determination of serum procaine-esterase by differential spectrophotometry.** L. Robert (*Experientia*, 1955, **11** [8], 316–317).—The method is based on the decrease of optical density at 295 mμ during hydrolysis. To determine the optical density of the mixture of serum and procaine, 0·1 ml is diluted with 5 ml of 0·1 *M* Na_2HPO_4 and water to 25 ml. The variation of the optical density determined at 295 mμ divided by $1{\cdot}28 \times 10^4$ gives the number of molecules of procaine hydrolysed. R. S. TONKS

See also Abstracts **330**, **339**, **514**, **527**, **564**, **581**, **616**.

Drugs

497. **Paper chromatography in pharmaceutical analysis. II.** J. Büchi and M. Soliva (Pharm. Inst., Eidg. Tech. Hochsch., Zürich, Switzerland) (*Pharm. Acta Helv.*, 1955, **30** [5–6], 195–210).—The feasibility of the separation of groups of pharmaceuticals by paper chromatography is discussed. By working with pH-buffered paper, a standard method for separating all acids and bases is theoretically possible, but there are many difficulties. The separation of 11 local anaesthetics and of 5 antihistamines has been studied. Water-saturated ether, or toluene - butanol - water (85 : 15 : 50) are the best solvents to use as mobile phase. The importance of the pH of the stationary phase is stressed. The identification of substances in the paper chromatograms may be carried out by measurement of R_F values, by spot tests applied to the paper, or by elution followed by characterisation of the purified eluate. Attempts are made to correlate R_F values with chemical and physical properties. A. R. ROGERS

498. **Polarographic titration of organic bases. I. Titrations with tungstosilicic acid.** M. Součková and J. Zýka (Karlovy Univ., Prague, Czechoslovakia) (*Československ. Farmac.*, 1955, **4** [4], 181–185).—A number of heteropolyacids were found to be suitable for the polarographic titration of organic bases. Though the polarography is complex, conditions for quantitative behaviour can be obtained easily. Tungstosilicic and tungstophosphoric acids are especially useful, as the reaction (particularly for alkaloids) is very sensitive and pptn. is immediate. The ppt. is frequently crystalline. The polarography also gives the composition of the tungstosilicic acid - organic base complex. Polarographic agents other than heteropolyacids include heavy-metal complexes, *e.g.*, $HPtCl_4$ and $HAuCl_4$, and iodo complexes of Pb and Hg; and organic acids forming addition products with the base concerned, *e.g.*, picric acid and alizarinsulphonic acid. The poor selectivity of tungstosilicic acid is due to its high sensitivity; this allows accurate determination of 10 to 20 mg of base. A 0·01 *M* aq. soln. of tungstosilicic acid ($0{\cdot}7SiO_2.12WO_3.24H_2O$) is used. The apparatus has a dropping-mercury cathode and S.C.E. anode, the voltage being 0·65 V. The pH of the soln. is adjusted with HCl (0·1 to 0·6 *N*). As the tungstosilicic acid is the only polarographically active component of the reaction mixture, the plot of current *vs.* acid added consists of two straight lines, the intersect being the equivalence point. The current remains almost constant till all the base has been removed and then increases linearly, owing to the presence of excess of tungstosilicic acid. The substances examined were the hydrochlorides of cocaine, narcotine, quinine, papaverine and procaine, and atropine sulphate, codeine phosphate, strychnine nitrate, amidopyrine, phenazone, cinchonine and narceine. The determination of each is discussed in detail, and a table summarising the optimum pH conditions, the composition of the ppt. ($SiO_2.12WO_3.x$ base), etc., for each alkaloid is given. The max. error is ± 1 per cent., except with papaverine hydrochloride (± 6 per cent.) and strychnine nitrate (method totally unsatisfactory); the constant error is −10 per cent. with phenazone (possibly owing to slight solubility of the titration product) and + 6 per cent. with narceine. **II. Titrations with tungstophosphoric and molybdophosphoric acids.** M. Součková and J. Zýka (*Ibid.*, 1955, **4** [5], 227–230).—When tungstophosphoric acid was used the apparatus had a dropping-mercury cathode and mercury anode, an e.m.f. of −0·4 V was applied and the titrations were carried out in 0·2 and 0·3 *N* HCl. The interpretation of the polarographic titration curves and the substances to which the method was applied are the same as for tungstosilicic acid. A table is given of the best media (in all but two instances, 0·25 *N* HCl), the composition of the reaction product ($P_2O_5.24WO_3.x$ base, where $x = 4$ or 5) and the weight range (5 to 50 μg) suited to the determinations. The method was unsatisfactory for cinchonine, narceine, atropine sulphate and procaine hydrochloride. For the other bases, errors are $< \pm 2$ per cent. Preferences are given for the use of tungstosilicic or of tungstophosphoric acid for the titration of each alkaloid examined. The results obtained by the two methods generally differ; only with cocaine and codeine are the compositions of the ppt. similar. This is in contradiction to the findings of Graf and Fiedler (*Arch. Pharm., Berlin*, 1953, **286**, 401). Molybdophosphoric acid was found to be unsuitable. A. O. JAKUBOVIC

499. **The scope of phenol - chloroform - acetonitrile as a solvent system in non-aqueous titrimetry.** L. G. Chatten (Food and Drug Directorate, Ottawa, Canada) (*J. Pharm. Pharmacol.*, 1955, **7** [9], 586–590).—Titration with 0·05 *N* perchloric acid in dioxan of 18 salts of organic bases in phenol - $CHCl_3$ - methyl cyanide can be done satisfactorily; this suggests a wider use of this solvent system, which offers advantages in respect of greater solubility and sharper end-points in many cases. The solubilities of morphine tartrate, morphine meconate, chlorothen citrate, sodium barbiturates, and the alkali-metal salts of carboxylic acids and of antibiotics are too small to permit use of this solvent system; halogen salts cannot be titrated because a side-reaction occurs; pyrilamine maleate gives no detectable end-point; the recovery of doxylamine succinate is not quantitative.
A. R. ROGERS

500. **A new approach to the determination of morphine in opium.** E. Brochmann-Hanssen (Univ. of Calif. Coll. of Pharm., San Francisco, Calif., U.S.A.) (*Medd. Norsk Farm. Selsk.*, 1955, **17** [4–5], 76–86).—A method for the determination of morphine (**I**) in opium, based on the use of ion-exchange resins, is described. It is shown that the calcium hydroxide method of U.S.P. XIV gives results that are about 25 per cent. low. *Procedure*—Extract the powdered sample (0·1 g) by shaking it with a suspension of Dowex $50–X_2$ (1 g in 25 ml of water) at 70° to 80° C for 15 min. Elute the resin with 4 *N* methanolic ammonia (50 ml). Pass the eluate through a column of Dowex $1–X_1$ previously activated by washing with methanolic ammonia. Wash with methanol (50 ml) and enough H_2O to remove the NH_3, then elute the amphoteric alkaloids, **I** and narceine (**II**), with 0·1 *N* HCl (50 ml). Determine **I** colorimetrically by the specific reaction with HIO_3 - $NiCl_2$ (*Anal. Abstr.*, 1955, **2**, 3093) or spectrophotometrically, after separation from **II** by the use of Amberlite IRC–50 at pH 7.
A. R. ROGERS

501. **The quantitative paper-chromatographic determination of morphine in opium.** A. B. Svendsen, E. D. Aarnes and A. Paulsen (Pharm.

Inst., Oslo Univ., Norway) (*Medd. Norsk Farm. Selsk.*, 1955, **17** [4–5], 116–123).—A paper-chromatographic method for the separation of morphine (**I**) from the other constituents of opium is described. When followed by a colorimetric determination of **I**, the method shows good agreement with the Ph. Helv. V assay for five samples of opium. *Procedure*—Triturate the sample (2·5 g) with conc. acetic acid (5 ml), mix with H_2O (25 ml), filter through sintered glass (Jena 3 G 3) and wash the ppt. with 5 per cent. acetic acid. Collect 50 ml of the filtrate. If necessary, purify further as follows: make the filtrate (25 ml) alkaline with aq. NH_3, and extract quant. with $CHCl_3$ - *iso*propyl alcohol (3:1); evaporate the extract to dryness, and dissolve the residue in 5 per cent. acetic acid (25 ml). Apply < 10 μl (containing 50 to 150 μg of **I**) to Whatman No. 1 filter-paper, equilibrate for 24 hr. and develop for 12 hr. with butanol - toluene - acetic acid - water (20:10:3:9, by vol.). Dry in air, cut out the **I** band, extract with diluted Folin - Ciocalteu reagent (0·3 ml of the original reagent in 5 ml of H_2O) for 2 hr., add 10 per cent. Na_2CO_3 (5 ml) and after 1 hr. measure the extinction at 700 mμ in a 1-cm cell. Alternatively, the cut-out **I** band may be sprayed with reagent, exposed to NH_3 vapour, and the colour determined *in situ* with an Elphor densitometer; the results are about 10 per cent. high by this technique.

A. R. ROGERS

502. **A suggested improvement in the U.S.P. method for determining morphine in opium.** H. W. Brickley and F. A. Whipple (Eli Lilly and Co., Indianapolis, Ind., U.S.A.) (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [9], 538–539).—The time taken for the U.S.P. XIV assay of opium may be reduced by a third by the addition of 25 per cent. of tribasic calcium phosphate to facilitate dispersion of the gum in the warm-water extractions and so speed up the subsequent filtrations. Recoveries of morphine from six samples of opium assayed by the U.S.P. method and by the proposed modified method were in good agreement. A. R. ROGERS

503. **Colorimetric determination of papaverine and its salts.** O. N. Soboleva (*Aptechnoe Delo*, 1955, **4** [4], 37–39).—When methylenedipapaverine, the condensation product of formaldehyde and papaverine (Freund and Fleischer, *Ber.*, 1915, **48**, 406), is treated with bromine water and then with aq. NH_3 soln., a greyish-violet ppt. is formed; the ppt. is soluble in ethanol and it can be extracted with chloroform, in which it forms a blue - violet soln. The reaction is specific for papaverine, being given by no other opium alkaloid. The sensitivity is 1 in 200,000. *Procedure*—A solution containing 0·5 to 1·5 mg of papaverine as hydrochloride is evaporated in a porcelain dish, and 2 drops of 35 per cent. formaldehyde soln. and 0·2 ml of conc. H_2SO_4 are added to the dry residue. The mixture is stirred for 30 min. and then transferred to a 25-ml glass-stoppered calibrated tube, the dish being washed with 0·5-ml quantities of water; 0·5 ml of bromine water is gradually added and, after being shaken, the tube is set aside for 4 min.; 5 ml of ethanol and 1 ml of 25 per cent. aq. NH_3 soln. are added and the soln. is made up to 25 ml with water. The colour is measured in an absorptiometer, with a blue filter. The error is $\pm$ 5 per cent.

E. HAYES

504. **Determination by infra-red spectrophotometry of papaverine and Dihydrone [dihydrohydroxycodeinone] simultaneously present in some galenical preparations.** B. Salvesen, L. Domange and J. Guy (Lab. Nat. de Contrôle des Médicaments, Faculté de Pharmacie, Paris) (*Ann. Pharm. Franç.*, 1955, **13** [5], 354–359).—Extracts from suppositories and ampoules containing papaverine and dihydrohydroxycodeinone (**I**) are made in $CHCl_3$ and the absorption is measured at 5·79 and 6·25 μ. At the former wavelength, **I** has the greater absorption and, at the latter, papaverine. The quantities of the two substances obtained from the calibration with pure substances are corrected by successive approximation. E. J. H. BIRCH

505. **The paper-chromatographic separation of the alkaloids in Tetrapon.** V. E. Krogerus, I. Rautiainen and B. Westerlund (Pharm. Inst., Univ. Helsinki, Finland) (*Medd. Norsk Farm. Selsk.*, 1955, **17** [4–5], 198–206).—The alkaloids (morphine, codeine, papaverine and narcotine) in Tetrapon may be satisfactorily separated by three alternative paper-chromatographic techniques: (*a*) two-dimensional, developing first with water-saturated *n*-butanol - acetic acid (5:1), then with a mixture of ether and 0·1 *M* acetic acid (5:2); (*b*) two-dimensional, developing first with dioxan - formic acid - water (90:0·5:9·5), then with *n*-butanol - acetic acid (5:1); and (*c*) successive development in the same direction with the two systems used in technique (*b*). A. R. ROGERS

506. **New reagents for the colorimetric determination of *Atropa* alkaloids.** F. M. Freeman (E. R. Squibb & Sons, Liverpool, England) (*Analyst*, 1955, **80**, 520–522).—Details of an absorptiometric method for the determination of atropine and related alkaloids are given. The well-known Vitali - Morin reaction was investigated with a view to improving the stability of the coloured complex formed, and it was found that the best results were obtained with tetraethylammonium hydroxide as the base and dimethylformamide as the solvent. The soln. (0·05 to 0·15 mg of alkaloid) is evaporated to dryness, nitrated with 0·2 to 0·3 ml of fuming HNO_3, again evaporated, dissolved in dimethylformamide, treated with 0·3 ml of 25 per cent. aq. tetraethylammonium hydroxide and diluted to 10 ml with dimethylformamide. The optical density is determined at 540 mμ in 1-cm cells against dimethylformamide, and the alkaloidal content is ascertained from a calibration graph, which is linear. The method is applicable also to phenylacetic acid, benzylpenicillin and benzathine penicillin, and in part to the determination of chloramphenicol. A. O. JONES

507. **The fluorimetric determination of the non-hydrogenated alkaloid content of hydrogenated ergotoxine-type alkaloids.** I. Gyenes, G. Szendei, B. Stefko and M. Németh (*Magyar Kém. Foly.*, 1955, **61** [8], 237–239).—Non-hydrogenated ergot alkaloids (**I**) show a blue fluorescence in filtered u.v. light, but hydrogenated ones do not. Dissolve the alkaloid (50 mg) in 1 per cent. ethanolic ethanesulphonic acid (2·0 ml) ($\not<$ 5 days old) and dilute to 200 ml with water at 25° C. Dilute a 30 to 40-ml sample to 50 ml with water, and determine in a Pulfrich fluorimeter the fluorescence at 25° $\pm$ 0·5° C, a Pulfrich D fluorescence standard being used. The content of **I** is obtained from a calibration curve. If < 2 per cent. of **I** is present, the results are approximate; if the concn. is 40 to 50 per cent., quenching occurs. The method is not suitable for coloured soln. A. G. PETO

508. **Determination of reserpine in pharmaceutical preparations.** R. E. Booth (Upjohn Co., Kalamazoo, Mich., U.S.A.) (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [9], 568–570).—A method for the determination of small quantities of reserpine (**I**) in commercial elixirs, based on the formation of a coloured complex with a dye, is described. Other fluid and dry formulations may be assayed similarly. Quaternary ammonium compounds, some antihistamines and certain other organic bases interfere. *Procedure*—Shake the sample (5 ml, containing $\simeq$ 0·25 mg of **I**) for 3 min. with $CHCl_3$ (50 ml), phosphate - citrate buffer (pH 4) (20 ml) and dye solution (5 ml) [bromophenol blue (200 mg) dissolved in H_2O (30 ml) and 0·1 *N* NaOH (6 ml) and diluted to 250 ml with H_2O]. Allow to separate and draw off the $CHCl_3$ layer. Carry out a further extraction with $CHCl_3$ (50 ml) and assay separately. The total **I** is given by the sum of the determinations in the two extractions. Measure the extinction at 402 mμ in 1-cm cells against $CHCl_3$ as blank, and calculate from a standard curve (one extraction only) prepared with the same batch of dye. By this method any reserpic acid (**II**) will be determined as **I**; if the percentage hydrolysis is required, **I** may be extracted from a mixture of the sample (5 ml) with 10 per cent. Na_2HPO_4 soln. (10 ml) by shaking the mixture with successive small portions of $CHCl_3$ (100 ml in all), and the **I** soln. free from **II** is assayed separately. A. R. ROGERS

509. **Analytical methods for reserpine.** W. H. McMullen, H. J. Pazdera, S. R. Missan, L. L. Ciaccio and T. C. Grenfell (Analytical Dept., C. Pfizer & Co., Inc., U.S.A.) (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [7], 446–453).—The physical properties of reserpine are discussed. Three methods of determination are described: (*i*) removal of reserpic acid by extraction from a $CHCl_3$ soln. with 0·01 *M* HCl, removal of trimethoxybenzoic acid by extraction with $NaHCO_3$ soln. and determining the extinction at 295 mμ and 268 mμ; (*ii*) heating the reserpine in strongly acid soln. and determining the extinction at 380 mμ; (*iii*) a fluorimetric procedure based on heating the reserpic acid in strongly acid soln., measuring the fluorescence and comparing it with that given by pure reserpine. G. R. WHALLEY

510. **The identification and determination of reserpine in tablets.** D. Banes (Food & Drug Admin., Div. Pharm. Chem., Washington, D.C., U.S.A.) (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [7], 408–411).—A method is suggested for the colorimetric estimation of reserpine (**I**) in tablets by means of a vanillin reagent; alternatively **I** may be hydrolysed and the resulting trimethoxybenzoic and reserpic acids determined. A weighed sample of tablets (containing the equiv. of 2·5 to 5 mg of **I**) is shaken with 25 ml of $CHCl_3$ for 3 min., then with 1-ml portions of a KH_2PO_4 soln. (136 g per litre) until the $CHCl_3$ forms a clear layer, which is removed. The tablet residue is twice extracted with two 10-ml portions of $CHCl_3$, and the combined extracts are diluted with 400 ml of *iso*octane. **I** is extracted with 30 ml of a citric acid soln. (2 g in 100 ml) followed by two further extractions with 10 ml, then 11 ml of ethanol are added to the combined extracts which are diluted to 110 ml; a 5-ml aliquot is diluted to 10 ml with water. This soln. and a standard containing 20 μg of **I** in 4 ml are treated with 2 ml of a vanillin reagent (500 mg in 25 ml of conc. HCl) and 6 ml of dil. H_2SO_4 (2 + 1); after 25 min., absorbancies are measured at 532 mμ. **I** may be determined by hydrolysis with NaOH soln. (10 per cent.). Reserpic acid is separated by extraction from acid soln. and determined as above with the vanillin reagent, whilst the trimethoxybenzoic acid in the $CHCl_3$ extract is determined from the u.v. absorption in ethanol at 240 mμ and 320 mμ. G. R. WHALLEY

511. **Assay of *Rauwolfia serpentina* preparations.** P. P. Pillay, S. B. Rao and D. S. Rao (Maharaja's Coll., Cochin, India) (*Indian J. Pharm.*, 1955, **17** [5], 95–97).—Variations in the alkaloidal content of rauwolfia from different sources are discussed. It is considered that the assay for total alkaloids prescribed in the B.P.C. is satisfactory for routine control only. A method of separating an "alkaloidal concentrate" consists in the extraction of powdered *Rauwolfia serpentina* root with hot alcohol, evaporating, and extracting the residue with water. The aqueous extract is clarified with the aid of Supercel and concentrated *in vacuo*. Aqueous NH_3 soln. is added to ppt. alkaloids, which are filtered off; a further ppt. is obtained by making the filtrate strongly alkaline with NaOH. The ppt. are combined and dried *in vacuo*. *Assay method*—Weigh accurately about 0·1 g of the alkaloidal concentrate into a stoppered flask and add $CHCl_3$ (25 ml), 95 per cent. ethanol (25 ml) and conc. aq. NH_3 (2 ml); shake for 1 hr. and transfer the mixture to a separating funnel; add ether (100 ml). Shake, then transfer the aqueous layer to a second separating funnel and wash with $CHCl_3$ (2 $\times$ 10 ml). Add the washings to the first funnel and extract the alkaloids with 0·5 *N* H_2SO_4. Make the extracts alkaline with aq. NH_3 and extract with $CHCl_3$, adding a small quantity of 0·1 *N* NaOH after the third extraction, then continuing extraction to completion. Wash the $CHCl_3$ extract with water and filter into a tared flask; distil off the solvent and dry the residue *in vacuo* to constant weight. H. B. HEATH

512. **The identification of digitoxin and digoxin from their acetyl compounds by means of paper chromatography.** S. Rohatgi (School of Pharmacy, Univ. Minnesota, Minneapolis, U.S.A.) (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [7], 428–431).—Digitoxin, α-acetyldigitoxin and β-acetyldigitoxin can be identified and differentiated by descending paper-chromatography with propane-1:2-diol as the stationary phase and a benzene - $CHCl_3$ mixture (9:1) as the mobile phase. For the separation of digoxin and α-acetyldigoxin, formamide is used as the stationary phase and a mixture of benzene and $CHCl_3$ (3:7) as the mobile phase. The advantage of a non-volatile stationary phase is that temp. variation has little effect, no saturation period is required and larger samples (30 to 40 μg) can be handled without "tailing." The Raymond reagent (*m*-dinitrobenzene and NaOH) is used to detect the spots; it gives a deep-blue colour with β-acetyldigitoxin and purple with the other compounds. A. R. ROGERS

513. **Assay of digitoxin.** W. Kussner, F. Reiff and H. W. Voigtländer (E. Merck, Darmstadt, Germany) (*Arch. Pharm., Berlin*, 1955, **288** [6], 284–298).—Purified samples of digitoxin (**I**) are used for the estimation of **I** and for the assay of gitoxin in samples of **I**. Commercial **I** is purified by passing it through columns of Al_2O_3 and eluting with $CHCl_3$ or mixtures of $CHCl_3$ and methanol, the final product being examined by paper chromatography. R_F values for **I**, digoxin and

gitoxin are 0·33, 0·75 and 0·61, respectively. For the estimation of **I**, 10 ml of a soln. containing 100 mg in 50 ml of methanol are diluted 1:10 with methanol. A 5-ml aliquot of this dilute soln. is treated with 15 ml of Baljet's reagent (1·8 g of picric acid dissolved in 50 ml of methanol and 20 to 30 ml of water, to which are added 12·5 ml of *N* NaOH and the whole made up to 100 ml) and allowed to stand at 20° ± 0·5° C for 20 min., when the absorption is measured at 490 mμ. Such measurements are repeated after a further 5 and 10 min., the highest extinction value being taken; a blank is similarly treated; $[E]^{1\%}_{1\,cm} = 231 \pm 4$. For the estimation of the gitoxin content of **I**, 100 mg of the dried substance are weighed into 2 ml of acetic acid, 5 ml of 2 *N* H_2SO_4 are added and the soln. is set aside at 20° C for 4 hr., when it is diluted with 5 ml of water and allowed to stand for 18 hr. at 10° to 15° C. The soln. is then neutralised with 10 per cent. aq. NaOH soln. (about 50 ml) and extracted several times with dichloromethane, the combined extracts being evaporated to dryness on a water bath. The residue, after being dried for 1 hr. at 100° C, is treated with 1·25 ml of HCl (d = 1·19) at room temp. for 1 hr. and finally dissolved in methanol and made up to 50 ml. The extinction of this soln., after dilution to 25 ml, is measured at 338 mμ.

G. R. WHALLEY

514. **The application of non-aqueous titrimetry to the determinations of cholic, deoxycholic and dehydrocholic acids.** R. Crisafio and L. G. Chatten (Food and Drug Lab., Dept. of Nat. Health and Welfare, Ottawa, Ontario, Canada) (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [9], 529–532).—Cholic, deoxycholic and dehydrocholic acids may be titrated potentiometrically with glass and calomel electrodes, or visually with thymol blue as indicator, in either benzene - methanol (10:1) or $CHCl_3$ - dimethylformamide (25:1) as solvents with either 0·1 *N* potassium methoxide soln. or 0·1 *N* methanolic KOH as titrant. These methods may be extended to the assay of commercial dehydrocholic acid tablets, and give results at least as satisfactory as those by the U.S. N.F.-IX method.

A. R. ROGERS

515. **Colorimetric method for the estimation of capsaicin in drugs.** K. E. Schulte and H. M. Krüger (Pharm. Inst., Freien Univ., Berlin) (*Z. anal. Chem.*, 1955, **147** [4], 266–270).—Capsaicin is estimated colorimetrically as the azo dye formed by coupling to it diazobenzenesulphonic acid. A preliminary separation of the capsaicin is made by adsorption chromatography. *Procedure*—The finely powdered pharmaceutical material (1 g) is introduced into an adsorption tube (20 cm × 1 cm) that contains 0·5 g of Al_2O_3 and 0·2 g of activated charcoal. On developing with 250 ml of 96 per cent. ethanol, all the capsaicin is extracted. The alcoholic extract is made up to 250 ml and a 5-ml aliquot is taken. The liquid is made alkaline with 1 ml of ≃ 0·2 *N* NaOH soln., and is treated with 1 ml of a 0·005 *M* soln. of diazobenzenesulphonic acid. Excess of the diazonium compound is destroyed by the addition of 1 ml of 0·005 *M* NaI soln., followed by heating the soln. for 5 min. in a water bath at 60° to 70° C. After being cooled, the soln. is made up to 10 ml with 0·2 *N* NaOH soln., and the determination is completed spectrophotometrically at 490 mμ. A blank is prepared from 5 ml of pure ethanol. By this method, 10 μg of capsaicin in 5 ml of alcoholic soln. can be determined quantitatively.

J. M. WATON

516. **Determination of phellandrene in essential oils.** G. Neirinckx and H. Struelens (*Ind. Chem. Belge*, 1955, **20** [8], 861–868).—Three methods for determining phellandrene (**I**) in essential oils were studied with a series of samples obtained by the fractionation of an oil from *Eucalyptus dives*: (1) gravimetric, by weighing the nitrosite formed with $NaNO_2$; (2) gravimetric, by weighing the addition product formed with maleic anhydride (**II**); and (3) a titrimetric method based on the reaction with **II**. The third method gave the most reliable results. A small (≃ 0·1 g) amount of sample is refluxed for 6 hr. at 100° C with 10 ml of a standardised solution of **II** in toluene. The cooled mixture is placed in a stoppered 250-ml Erlenmeyer flask and to it are added 15 ml of 25 per cent. aq. KI soln., 15 ml of 4 per cent. aq. KIO_3 soln., and a measured excess of 0·1 *N* aq. $Na_2S_2O_3$. The excess of **II** (which has not reacted with **I**) is hydrolysed to maleic acid, which liberates an equiv. amount of I from KI + KIO_3; the excess of $Na_2S_2O_3$ is titrated with 0·1 *N* iodine solution, and the **I** content of the original sample is calculated from the result.

S.C.I. ABSTR.

517. **A note on the determination of ascaridole in oil of chenopodium.** A. H. Beckett and G. O. Jolliffe (*J. Pharm. Pharmacol.*, 1955, **7** [9], 606–607).—Beckett and Jolliffe (*cf. Anal. Abstr.*, 1954, **1**, 361) gave a quadratic expression relating titre of thiosulphate to weight of ascaridole (**I**) for the B.P. method for the determination of **I** in chenopodium oil. The equivalents are now tabulated for rapid calculation.

A. R. ROGERS

518. **Applications of chromatography. XXII. Chemical assay of insulin preparations.** Masaharu Yamagishi, Toru Masuda, Makoto Yokoo, Mitsuko Asai and Satoru Kuwada (Takeda Pharm. Ind., Osaka) (*Pharm. Bull., Japan*, 1955, **3** [1], 1–4).—The sample is purified by electrophoresis, the band containing the insulin is eluted, the eluate is subjected to a micro-Kjeldahl digestion and the nitrogen is estimated. Apply 0·05 ml of an approximately 1 per cent. solution of insulin in 0·05 *N* HCl to each of two filter-papers (2 cm × 42 cm) and subject to electrophoresis for 5 hours, using a potential of 300 V and a Theorell buffer (pH 9 to 11) of ionic strength 0·07. The insulin migrates about 4 cm towards the anode; determine its exact position on one of the papers, by the use of bromophenol blue (*cf.* Durrum, *Brit. Abstr. C*, 1952, 15), cut out the corresponding band on the other paper, and elute with 10 ml of H_2O. Digest the eluate by a micro-Kjeldahl method and determine the nitrogen. It is claimed that insulin is separated from other proteins and that agreement with biological assays is obtained in the analysis of samples containing ≮ 15 international units per mg.

P. S. STROSS

519. **Microbiological assay on large plates. III. High-throughput, low-precision assays.** K. A. Lees and J. P. R. Tootill (Glaxo Laboratories, Ltd., Stoke Poges, Bucks., England) (*Analyst*, 1955, **80**, 531–535).—A series of designs is given for assays when only moderate precision (standard error ≃ ± 10 per cent.) is required, but when the number of samples to be simultaneously assayed is usually more than 10. These designs fall into two types: (I) a completely random arrangement and (II) Youden squares and balanced lattice squares.

Type I is applicable to plate assays where inherent inaccuracies occur (*e.g.*, with vitamin B_{12}), type II is applicable when inherent inaccuracies are less (*e.g.*, with antibiotics), and although no great precision is required in preliminary work the removal of error from temporal and positional effects is worth while. Designs for this type fall into two classes—those in which the confounding is confined to one dimension (Youden squares) and those in which the confounding is equal in two dimensions (balanced lattice squares). The latter class is particularly suitable with a large number of solutions when only comparison of the potencies with that of a standard is required. Examples of these two types and classes are given.

A. O. JONES

520. **Metal chelate compounds with tetracycline derivatives. II. Colorimetric determination of aureomycin [chlortetracycline] with quadrivalent thorium.** Takeichi Sakaguchi and Kiyomi Taguchi (Pharm. Inst., Univ. Chiba, Japan) (*Pharm. Bull., Japan*, 1955, **3** [3], 166–170).—Two slightly different methods for the estimation of chlortetracycline, based on the chelation of Th$^{\cdots\cdot}$, are described. *Procedure*—(*i*) Dilute an aliquot (0·25 to 2·0 ml) of a 0·05 per cent. solution of chlortetracycline hydrochloride in a 25-ml calibrated flask to 20 ml with water, neutralise with 0·05 *N* NaOH and add 2 ml of sodium acetate buffer (35 ml of 0·2 *M* sodium acetate with 165 ml of 0·2 *M* acetic acid) followed by 1 ml of $Th(NO_3)_4$ solution [1 g of $Th(NO_3)_4$ in 20 ml of H_2O adjusted to pH 4·0 and diluted to 100 ml with the acetate buffer], and make up to 25 ml with water. Allow to stand for at least 20 min., measure the extinction at 405 mμ and compare with a standard. From 5 to 40 μg can be determined, but PO_4''', SO_4'' and F′ interfere. (*ii*) To 1 ml of a 0·05 per cent. chlortetracycline hydrochloride solution add 0·5 per cent. aq. $Th(NO_3)_4$ solution (0·5 ml) and dilute to 3 ml with H_2O; add 2 *N* HCl (5 ml), heat on a boiling-water bath for 5 min. and dilute to 25 ml with H_2O. Measure the extinction at 450 mμ after 15 min. and compare with a standard. **III. Colorimetric determination of aureomycin [chlortetracycline] with boric acid.** Takeichi Sakaguchi (*Ibid.*, 1955, **3** [3], 170–173).—Of the two methods given it is stated that the following gives more satisfactory results. To an aliquot (0·5 to 2·5 ml) of an approximately 0·05 per cent. solution of chlortetracycline (**I**) in H_2O add boric acid - sulphuric acid mixture (2 ml) [10 g of boric acid dissolved in 100 ml of H_2SO_4 (sp. gr. 1·84)], dilute to 20 ml with H_2SO_4 (sp. gr. 1·84) and heat at 80° ± 3° C for 5 min. Cool, make up to 25 ml with H_2SO_4 (sp. gr. 1·84), measure the extinction at 530 mμ after 2 hr. and compare with a standard. To avoid interference, extract the **I** from aqueous solution, after saturating it with Na_2SO_4, with small portions of *iso*butyl alcohol at pH 3 to 5; evaporate the *iso*butyl alcohol and proceed as above.

P. S. STROSS

521. **Coupling reactions of *p*-diazobenzenesulphonic acid. I. Photometric determination of some drugs.** A. Berka and J. Zýka (Karlovy Univ., Prague, Czechoslovakia) (*Českosl. Farmac.*, 1955, **4** [5], 225–227).—The photometric determination of a number of phenols and amines [*viz*, phenol, resorcinol, 2-naphthol, arbutin, sulphathiazole and Analeptine (phenylephrine)] was carried out by examining the spectra of the substances when coupled with *p*-diazobenzenesulphonic acid (**I**). Temperature and pH must be carefully controlled. A buffer (pH 9·2) is used and the temp. is kept at ≃ 5° C. If a large excess of **I** is used the coupling is rapid, but even a slight excess allows the reaction to be completed in an hour and the colour does not change in intensity even after 24 hr. Maximum absorption is at ≃ 450 mμ in all cases.

A. O. JAKUBOVIC

522. **Complexiметric determination of bromoform in syrups.** M. Šaršúnová and Čičmancová (Dist. Control Lab. Bratislava Medica, Czechoslovakia) (*Českosl. Farmac.*, 1955, **4** [4], 187–188).—The method consists in saponification of the bromoform and precipitation of the bromide thus formed with an excess of $AgNO_3$ soln. The AgBr is dissolved in an excess of aq. NH_3 soln. and $K_2Ni(CN)_4$ is added. The Ag complexes with the cyanide and the liberated Ni is titrated with EDTA (disodium salt), with murexide as indicator. The method is suitable for the determination of bromoform alone or in syrups. The error is < ± 0·6 per cent.

A. O. JAKUBOVIC

523. **Determination of the amount of *m*-aminophenol in sodium PAS [4-aminosalicylate] by the French Codex method.** J. Morise (Lab. Grémy, Paris) (*Ann. Pharm. Franç.*, 1955, **13** [5], 333–349).—The method of Pesez (*Bull. Soc. Chim. Biol., Paris*, 1949, **31**, 1369), in which the entire material is diazotised in aq. solution, when the *m*-aminophenol couples with the 2:4-dihydroxybenzoic acid formed by decomposition of the diazotised 4-aminosalicylic acid to give a coloured solution, is compared with the method due to Sanz in the Supplement (1953) to the French Codex, 1949, in which the *m*-aminophenol is separated by ether pptn. of the 4-aminosalicylate from methanolic solution, and is then coupled with diazotised *p*-nitroaniline. The Pesez method never shows less than 0·2 per cent. of *m*-aminophenol owing to interference, and for small quantities the Sanz method is more accurate. Since the actual absorption in the Sanz method depends on the presence or absence of both ether and peroxide, the standard solution in methanol, made up according to the Codex, is unsatisfactory. The Pesez method has the advantage that it is equally applicable to aq. solutions and to the solid material.

E. J. H. BIRCH

524. **Experimental data on the determination of *m*-aminophenol in 4-aminosalicylic acid according to the method of Pesez. Application to pharmaceutical preparations.** A. Sezerat (Services de Recherches Uclaf-Roussel, Paris) (*Ann. Pharm. Franç.*, 1955, **13** [5], 350–353).—In Pesez's method for the determination of *m*-aminophenol in 4-aminosalicylic acid (**I**) (*cf. Anal. Abstr.*, 1956, **3**, 523) there is always a background colour which makes it necessary for standard and blank to contain equal quantities of **I**. Other modifications suggested are larger volumes of solution and a short standardised time of contact in acid solution to avoid decarboxylation of **I**. The aq. solution of **I** is diluted to 1 mg per ml, and 5 ml are placed in a 100-ml flask and diluted to 50 ml at 0° C. After 10 min., 2 ml of 10 per cent. H_2SO_4 and 2 ml of 1 per cent. $NaNO_2$ solution, also at 0° C, are added and, after 3 min., 20 ml of 10 per cent. Na_2CO_3 solution. After 15 min. at room temp., the solution is made up to 100 ml and the absorption is measured at 336 mμ. The standards and blank are similarly prepared.

E. J. H. BIRCH

525. **A new spray reagent for paper chromatography of barbiturates.** E. Hjelt, K. Leppänen and V. Tamminen (Institute of Forensic Medicine, University of Helsinki, Finland) (*Analyst*, 1955, **80**, 706–707).—Barbiturates are separated by ascending paper-chromatography on paper impregnated with *M* KNO_3, *n*-butanol - pentanol - aq. NH_3 being used as solvent (*cf.* Hübner *et al.*, *Anal. Abstr.*, 1955, **2**, 174). The paper is kept in a solvent atmosphere for at least 6 hr., the time for chromatography being $\simeq$ 18 hr.; mixtures are kept for 12 to 14 hr. in the solvent atmosphere. After development, the dried paper is sprayed with a 1 per cent. soln. of $Co(NO_3)_2$ in absolute ethanol, dried again and held in NH_3 vapour. To achieve exact definition of the spot limits the paper is sprayed with an aq. soln. containing 200 mg of $CuSO_4$, 2 ml of pyridine and 20 mg of quinine per 100 ml. The dried paper is then held in HCl vapour. In u.v. light the barbiturates are visible against the fluorescent background as dark-blue spots or circles. Finally the paper can be treated with $KMnO_4$ to indicate unsaturated barbiturate derivatives. A. O. JONES

526. **The determination of barbiturates in pharmaceuticals.** F. A. Rotondaro (Food and Drug Admin., Philadelphia, Pa., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [3], 809–820).—The sample, containing 100 to 150 mg of barbiturate (for gravimetric or volumetric determination) or 15 to 30 mg (for spectrophotometric determination), is treated with 10 to 15 ml of water, acidified with HCl and extracted with 15 to 25 ml of chloroform. The chloroform layer is then shaken successively with (*a*) 1 g of $NaHCO_3$ in 10 to 15 ml of H_2O with 3 to 4 drops of 10 per cent. HCl (pH 7·2 to 7·5), (*b*) and (*c*) 10 ml of 0·1 *N* NaOH, (*d*) 5 to 10 ml of water. Pure barbituric acid is retained in the aqueous phase in (*b*), (*c*) and (*d*). For spectrophotometric determination the combined alkaline solutions are diluted to contain 1 to 2 mg per 100 ml, extinction measurements being made at pH 10·5 to 11·5. Alternatively, the combined alkaline solutions can be titrated with $AgNO_3$ soln.; the acids can be titrated in 15 per cent. HCl with Br (followed by identification of the bromo derivative by m.p.) or the extracted acid can be titrated with alkali, and the barbituric acid obtained from the alkalimetric determination can be weighed. The combined alkaline solution, or the barbiturate extracted from it, may be used for the chromatographic separation or determination of two or more barbiturate derivatives.
A. A. ELDRIDGE

527. **A note on the paper-chromatographic separation of phenobarbitone metabolites.** A. S. Curry (Forensic Sci. Lab., Harrogate, England) (*J. Pharm. Pharmacol.*, 1955, **7** [9], 604–605).—A phenobarbitone metabolite has been detected in urine extracts. It gives a band with $R_F = 0{\cdot}17$ when examined by the paper-chromatographic method of Algeri and Walker (*cf. Brit. Abstr. C*, 1952, 349), with butanol - aq. NH_3 as solvent and mercuric sulphate - diphenylcarbazone as developer; the absorption shows $\lambda_{min.} = 232{\cdot}5$ mμ and $\lambda_{max.} = 249{\cdot}5$ mμ at pH 13, although the spectra are otherwise generally similar to those of barbiturates.
A. R. ROGERS

528. **Coulometric determination of *iso*nicotinic acid hydrazide [isoniazid] by electrochemical oxidation with chlorine.** K. Kalinowski (Med. Acad., Lodz, Poland) (*Przem. Chem.*, 1954, **10**, 73–74).—Chlorine liberated by electrolysis of 10 per cent. aq. HCl, which also serves as electrolyte, oxidises directly isoniazid present in the anode compartment. The anode compartment is separated from the cathode by an asbestos sheet and contains methyl red, decolorisation of which by excess of chlorine marks the end of the reaction. Platinum-wire electrodes and a current density of 10 mA per sq. cm are used. A milliammeter and iodine coulometer are placed in series with the electrolysed soln. The liberated iodine is titrated with 0·01 *N* $Na_2S_2O_3$ (1 ml of $Na_2S_2O_3 \equiv 0{\cdot}34285$ mg of isoniazid). The error is $\pm$ 0·3 per cent.
A. O. JAKUBOVIC

529. **Complexiметric titrations in pharmaceutical analysis. XI. Indirect determination of hexamine and isoniazid.** B. Buděšínský (United Pharm. Ind., Prague, Czechoslovakia) (*Českosl. Farmac.*, 1955, **4** [4], 185–186).—Both hexamine (**I**) and isoniazid (**II**) react quantitatively with $Cd(SCN)_2$ at pH 6 to 7, giving the complexes $[Cd_2(C_6H_{12}N_4)](SCN)_4$ and $[Cd(C_6H_7N_3O)](SCN)_2$, respectively. The determination consists in back-titrating the excess of standard thiocyanate solution after filtering off the pptd. complex. When **I** is being determined the amount in excess and the time taken affect the determination but, with **II**, neither of these nor temp. affects the determination; this is an improvement on the current oximetric methods. *Procedure*—**I** (0·1 to 0·3 g) is dissolved in 15 ml of water and made up to 25 ml with 0·5 *M* $Cd(SCN)_2$ soln. After the soln. has been filtered, 10-ml portions are used to back-titrate the excess of thiocyanate. For the determination of **II**, 0·1 to 0·5 g is used, and the soln., together with 20 ml of 0·25 *M* $Cd(SCN)_2$, is made up to 100 ml. Data show that errors are always negative and generally $< 0{\cdot}8$ per cent.
A. O. JAKUBOVIC

530. **Gravimetric determination of chlorpromazine.** J. Blažek and Z. Stejskal (State Inst. for the Control of Med., Prague, Czechoslovakia) (*Českosl. Farmac.*, 1955, **4** [5], 246–247).—The solution containing $\simeq$ 20 mg of chlorpromazine is diluted to 20 ml with water and heated to 70° C. One ml of 35 per cent. HCl soln. is added, and 8 ml of 10 per cent. tungstosilicic acid are added, dropwise, while the soln. is stirred. The ppt. is dried at 110° C. The percentage of chlorpromazine is given by the expression $\frac{30{\cdot}65x}{y}$, where x = wt. (g) of dried ppt. and y = volume (ml) of the medicinal soln. used.
A. O. JAKUBOVIC

531. **Paper-chromatographic detection of potassium 8-hydroxyquinoline sulphate in tobacco.** E. Wegner (*Z. LebensmittUntersuch.*, 1955, **102** [1], 34–37).—A preparation of this chemical is sold under the name "Chinosol" for the preservation of tobacco against mould growth. The method described depends on the chromatographic identification of 8-hydroxyquinoline (**I**) in a steam-distillate ($\simeq$ 200 ml) from the tobacco (25 g). The distillate is made alkaline with NaOH and extracted with ether to remove the nicotine; the aq. phase is then neutralised, treated with an excess of $NaHCO_3$, and extracted with ether. The combined ethereal extracts are dried with Na_2SO_4 and evaporated to dryness under reduced pressure. The residue containing the **I**, if present, is dissolved in 2 ml of ethanol for chromatographic analysis, with either aq. 15 per cent. acetic acid or 0·067 *M* phosphate buffer of pH 6·25 as ascending solvent. When the

latter solvent is used, the paper is saturated with the buffer, and dried before use. Identification tests include spraying with aq. $FeCl_3$ or Dragendorff's reagent, exposure to iodine vapour, and a fluorescence test. P. S. ARUP

532. **Complexiметric titration in pharmaceutical analysis. XII. Indirect determination of some 8-hydroxyquinolines.** B. Buděšínský (United Pharm. Ind., Prague, Czechoslovakia) (*Českosl. Farmac.*, 1955, **4** [5], 221–222).—The method depends on an excess of metal ions added to soln. of 8-hydroxyquinolines thus pptg. the complex. The excess of cations is then back-titrated. Zinc (as 0·05 *M* $ZnSO_4$) was found to be the most suitable metal. For 8-hydroxyquinoline, 5:7-dichloro-8-hydroxyquinoline and 5-chloro-8-hydroxyquinoline the pptn. is quant. at pH 10. For 8-hydroxyquinolinesulphonic acids, soln. of higher concn. must be used, and an acetic acid buffer of pH 4 is best as the pptn. medium. The excess of Zn is titrated with 0·05 *M* EDTA (disodium salt), with Eriochrome black T or catechol violet as indicator (the former indicator is preferred). A table of results shows the max. error to be 2 per cent., but in 87 per cent. of the results quoted the error is $< \pm 1$ per cent. A. O. JAKUBOVIC

533. **Partition chromatography of sulphonamides on paper impregnated with a buffer.** D. Rybář, B. Toušek and I. M. Hais (Chemopharma, Ústi nad Labem, Czechoslovakia) (*Chem. Listy*, 1954, **48** [10], 1532–1536).—The influence of pH on the separation of a number of sulphonamides by chromatography on paper (Whatman No. 1) impregnated with borate buffers, with *n*-butanol saturated with water as the mobile phase, was investigated. The dissociation of the sulphonamido group at higher pH and the ionisation of the aromatic amino group of the sulphonamides at lower pH leads to a lowering of their R_F values. The relationship between R_F or R_M values and pH is dependent on the p*K* values of the sulphonamides, but even at extreme values of pH no simple relationship has been established. By choosing a suitable buffer, the separation of sulphonamides by paper partition chromatography is readily achieved. G. GLASER

534. **Analysis of sulphonamides.** J. Vulterin and J. Zýka (Katedra anal. chem. Karlovy univ., Prague, Czechoslovakia) (*Chem. Listy*, 1954, **48** [11], 1696–1698).—In strongly alkaline media (15 to 45 per cent. KOH), sulphonamides with a primary amino group give an orange to red coloration on treatment with 0·1 *M* $K_3Fe(CN)_6$. The reaction, although less sensitive than the usual diazotisation and coupling methods, can be used for the detection and determination of sulphonamides. Maximum extinction is obtained after 2 min. with absorption max. at 420 mμ. G. GLASER

535. **Electrophoretic separation of sulphonamides.** A. Okáč and V. Jokl (Inst. of Anal. Chem., Faculty of Nat. Sci., Brno, Czechoslovakia) (*Českosl. Farmac.*, 1955, **4** [5], 219–220).—The electrophoresis of a number of commercial sulphonamides was carried out on paper strips (10 cm × 27 cm), with an e.m.f. of 120 V, and H_2SO_4, NaOH, and various buffer solutions to give electrolytes of pH from 1 to 13. The detection (after 2 to 5 hr. of current flow) of the separated sulphonamides was carried out with a soln. of 1 per cent. *p*-dimethylaminobenzaldehyde in 3 per cent. HCl, as detection by diazotisation was not achieved. The mobilities obtained are not absolute, and endosmosis of the electrolyte towards the cathode at pH > 4·7 must also be taken into account. The largest mobility differences were found in alkali soln., a borate buffer of pH 8·5 being particularly useful for the separation. A. O. JAKUBOVIC

536. **Application of different viscosity functions to the analysis of technical dextran.** K. Zakrzewski, K. Murawski, J. Malec, Z. May and J. Krysiak (Haematol. Inst., Warsaw) (*Przem. Chem.*, 1954, **10**, 209–211).—Medicinal dextran must be of fixed mol. wt. This is controlled by measurement of viscosity which is a function of mol. wt. and structure. $[\eta] = kM^a$; $[\eta]$ is found by measurement of viscosity at various concentrations and extrapolating to zero concn. Different graphs are obtained depending on the function of viscosity used. With Kraemer's function, $[\eta] = \lim\ (c \to 0)\ \frac{\eta_r}{c}$, points lie on a straight line for concn. up to 1 per cent. The Philipoff function $\eta_r = \left[1 + \frac{[\eta]c}{8}\right]^8$ gives the least satisfactory results. Martin's empirical equation was also applied. The best results are obtained when the coeff. of variation is 4·82. The intrinsic viscosity can be obtained for a given dextran sample from a single measurement with satisfactory exactness from the formula $[\eta] = \frac{\ln \eta_r}{c}$, when $c \leqslant 1$. A. O. JAKUBOVIC

537. **Determination of sodium carboxymethylcellulose.** C. R. Szalkowski and W. J. Mader (Chem. Div., Merck & Co., Inc., Rahway, N.J., U.S.A.) (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [9], 533–535).—The method described for the determination of Na carboxymethylcellulose (**I**) in antibiotic preparations is based on pptn. of the calcium salt and colorimetric estimation with 2:7-dihydroxynaphthalene. Formaldehyde and glycollic acid interfere. The precision (coefficient of variation) and accuracy are better than ± 2·5 per cent., but the method is too slow for routine use. *Procedure*—Dissolve the sample (containing 2 to 4 mg of **I**) in H_2O (50 ml) and adjust the pH to 2·5 with 10 per cent. HCl. Add 1 per cent. aq. $CuSO.5H_2O$ soln. (50 ml), stir the soln. well and adjust the pH to 4·1 with 3 per cent. aq. NH_3 soln. (added dropwise). After 1 hr., filter through sintered glass. Wash the ppt. with several 10-ml portions of H_2O and dissolve it in warm 60 per cent. H_2SO_4 (50 ml). To a 2-ml aliquot of the cooled soln. in a stoppered tube (2·5 cm × 20 cm) add the reagent (10 mg of 2:7-dihydroxynaphthalene in 20 ml of conc. H_2SO_4, set aside in the dark for 4 18 hr. before use), shake and heat the soln. on a bath of boiling water for 3 hr. Cool the soln. in an ice box for 5 min., add 60 per cent. H_2SO_4 (20 ml) and, after 30 min., measure the extinction at 530 mμ against a reagent blank. A calibration curve is prepared from **I** of the same degree of substitution as that in the sample. A. R. ROGERS

538. **The determination of potassium and sodium in compound injections. A titrimetric - gravimetric method.** R. Klevstrand (*Medd. Norsk Farm. Selsk.*, 1955, **17** [4–5], 190–197).—Methods have been developed for the determination of Na and K in the presence of chloride, phosphate and lactate in compound injection soln. approx. 0·05 *N* in K^+ and 0·1 *N* in Na^+. Total salt is determined by titration

with 0·1 *N* HCl or 0·1 *N* NaOH after passage through a column of Dowex-2 resin or Amberlite IR-120, respectively, methyl red being used as indicator. Potassium is determined gravimetrically by pptn. with Na tetraphenylboron. If the anion-exchange resin is used, results are about 2 per cent. low in the presence of lactate, but pptn. of K may be carried out in the titrated soln. from the first assay. A. R. ROGERS

539. **General data on the investigation of arsenic in toxicology. The examination of hair.** H. Griffon (*Ann. Pharm. Franç.*, 1955, **13** [4], 258–283).—The investigation necessary in the determination of arsenic in toxicology is reviewed, and notes on methods of sampling from recent and decomposed corpses, and burial soil are given. The importance of the determination of arsenic both chemically and physically (by radioactivity) at intervals along the hair is discussed, and curves are given which are typical of long-standing and acute poisoning. The variation of individual rates of growth of hair is discussed, but it is shown that mechanical lengthening of the hair in life by combing is improbable. The so-called diffusion of arsenic along the hair is partly accounted for by the covering of the hair with the natural secretion of the skin, and this may be removed by preliminary degreasing. With decomposed corpses, contamination by liquids from the corpse is avoided by washing in water, HCl, acetone and alcohol, which do not remove arsenic incorporated into the hair during growth. Arsenic may be detected in the hair 10 to 24 hr. after ingestion. E. J. H. BIRCH

See also Abstracts 442, 447, 449, 563, 568.

Food

540. **Cold-water-soluble starches. II.** E. Dux (*Stärke*, 1955, **7**, 81–86).—Cold-water-soluble starches (**I**), produced by the drum-drying of suitable pastes, were examined and it was found that the presence of free NaOH during processing caused some interference with well-established methods of assay of these products. (1) Determination of the alkali number (according to Schoch) gave low values, owing to the presence of NaOH, which had combined with starch during drying, limiting further uptake of NaOH during alkaline digestion. Correct values were obtained by acidifying the starch solution to pH 3, then adjusting to pH 7, before the determination of alkali number. (2) Alkaline **I** were found to be somewhat soluble in ethanol, *e.g.*, 3·5 per cent. of the starch being soluble at a NaOH content of 10·2 per cent. Ethanol should therefore not be used in the quant. determination of these substances. (3) The **I** were produced by four different methods, including spray-, drum- and vacuum-drying of starch solutions and pptn. by ethanol. Measurements of the reducing value and alkali number gave information on the method of preparation of **I** and it was found that development of solubility in cold water need not necessarily be accompanied by depolymerisation of the starch molecules. E. DUX

541. **Factors affecting the determination of sugar in beets by the Sachs - Le Docte method.** E. H. Hungerford and C. R. Koontz (*Proc. Amer. Soc. Sug. Beet Tech.*, 1954, **8** [2], 303–309).—Five methods for determining sugar in beets were tested and 50 determinations were made by the Sachs - Le Docte cold-digestion method, the Sachs - Le Docte hot-digestion method, the Soxhlet method, the Pellet method with lead added before digestion, and the Pellet method with lead added after digestion and cooling. The results by the Sachs - Le Docte method with 177 ml of lead acetate soln. (2·15° Brix) and cold digestion agree closely with those by the same method, using 178·4 ml and hot digestion, and also with those by the Soxhlet method. The vol. of the flask for the Pellet method should be 201·6 ml. SUGAR IND. ABSTR.

542. **Biochemical determination of sugars in foodstuffs.** F. T. van Voorst (*Stärke*, 1955, **7**, 105–107).—A new method for the determination of carbohydrate constituents of starch syrups and similar foodstuffs is described. Selective fermentation of groups of sugars by yeast is followed by estimation of the remaining non-fermented sugars. The yeast *Saccharomyces cerevisiae* ferments monosaccharides (glucose) and maltose, but not lactose and oligosaccharides. *Candida pseudotropicalis* (*Torula cremoris*) ferments only monosaccharides and lactose, but not maltose. The two yeasts are allowed to act separately and jointly on the sugar mixture for 14 hr., followed by estimation of the remaining sugars with Luff's copper reagent. From the results obtained each of the following sugars may be determined in any mixture containing them: fructose, glucose, lactose, maltose, reducing dextrins, non-reducing dextrins and sucrose. For dextrins, acid hydrolysis of the sugars remaining after fermentation is required, followed by determination of the liberated glucose. Details of the calculation, but only a few experimental details and no indication of the accuracy obtained, are given. E. DUX

543. **Design and operating technique of a vacuum drying oven. III. Solids in (*a*) mixtures of cane and beet molasses and (*b*) beet molasses.** S. D. Gardiner and F. J. Farmiloe (Tate and Lyle Res. Lab., Keston, Kent, England) (*Analyst*, 1955, **80**, 557–561).—The method described in Part II (*cf. Anal. Abstr.*, 1954, **I**, 2802) for the determination of true solids in cane molasses by vacuum drying, or by refractive index corrected for ash and invert products, has been extended to include their determination in beet molasses and in mixtures of cane and beet molasses. For beet molasses an equation relating true solids to apparent solids (deduced from the refractive index by means of sucrose tables), invert sugar and sulphate ash has been derived. Separate determinations of K and Na by flame photometer (as are necessary with cane molasses) were not found necessary for greatest accuracy with beet molasses. The necessary corrections to the refractive index figures for mixtures of cane and beet molasses are tabulated.
A. O. JONES

544. **Gerber method for the determination of fat in milk and milk products. I. Apparatus.** British Standards Institution (2 Park Street, London) (B.S. 696: Part 1:1955, 32 pp.).—The earlier Standard, B.S. 696:Part 1:1936 (*cf. Analyst*, 1936, **61**, 769), has been revised. The milk pipette is now required to be calibrated to deliver 10·94 ml of water and wider tolerances are allowed for automatic pipettes for measuring H_2SO_4 and amyl alcohol. Other new details include plain or corrugated necks for Gerber butyrometers; circular bore or "flat scale" pattern of graduated tubes for Gerber butyrometers for testing milk, cream and cheese; and normal working tolerances for certain

dimensions of the apparatus. Important requirements for centrifuges are given and details of an automatic mercury pipette for Gerber-tube calibration. **II. Methods.** British Standards Institution (B.S. 696: Part 2: 1955, 16 pp.).—Methods for testing milk and milk products as published in B.S. 696: Part 2: 1936, have been revised. A new temperature of 65° ± 2° C is specified for final temperature adjustment. For ordinary milk, no heat need be applied before centrifuging and scale corrections for fat readings are tabulated; for cream testing, the addition of hot water is specified. A new section is included for homogenised and sterilised milk.

D. G. FORBES

545. **"Ratio of volatile acidity," a new analytical index for butter.** G. Curli (*Chim. e Ind.*, 1955, **37** [8], 628–630).—The melted and filtered fat (5 g) is saponified, acidified and distilled, as for a Reichert value, two 65-ml fractions being collected, each in 20 to 21 min. The ratio of the acidities of the first and second fractions is determined. Butter gives a value of 2·03 to 2·13, hydrogenated dolphin oil 4·0 to 4·1, coconut oil 1·1 and margarine containing triacetin 0·8. L. A. O'NEILL

546. **A study of methods of testing and sampling for the determination of fat content of ground meat.** D. C. Kelley, R. E. Guerrant and D. L. Mackintosh (Kansas State College, Manhattan, Kansas, U.S.A.) (*Food Tech., Champaign*, 1954, **8**, 273–276).—The fat content of ground meat may be determined rapidly by a modified Babcock method, H_2SO_4 and centrifuging being used. The results agree well with those by the ether-extraction (A.O.A.C.) method. Complete mixing and grinding of the sample is important with all methods. Seasoning added to pork sausage meat interferes with the accuracy. The use of Minnesota reagent (Na salicylate, K_2CO_3, NaOH and *iso*propyl alcohol) instead of H_2SO_4, or the omission of the centrifuging, leads to variable results. *Procedure*—Disperse the sample (9 g) in H_2O (5 ml) in a Paley bottle at 70° C. Add glacial acetic acid (5 ml) and conc. H_2SO_4 (15 ml) and allow to digest for 2 to 3 min. Centrifuge at 1000 r.p.m. for 5 min., warm to 70° C for 2 min., add H_2O at 70° C to bring the meniscus into the graduated stem, centrifuge at 800 r.p.m. for 2 min., warm at 70° C for 2 min., and measure the volume of the fat layer.

A. R. ROGERS

547. **Use of the 2-thiobarbituric acid reagent to measure rancidity in frozen pork.** E. W. Turner, W. D. Paynter, E. J. Montie, M. W. Bessert, G. M. Struck and F. C. Olson (Oscar Mayer & Co., Madison, Wisconsin, U.S.A.) (*Food Tech., Champaign*, 1954, **8**, 326–330).—A method in which 2-thiobarbituric acid (**I**) reagent is used to determine rancidity in frozen pork gives a more reliable index of the age and quality than other chemical tests. The small amounts of naturally occurring carbohydrates present in fresh pork tissue do not interfere, but correction must be made for sugars present in cured meats and sausage products. A significant positive correlation was obtained between palatibility of wieners and pork patties and the **I** value of the pork used. *Procedure*—Prepare the sample by grinding twice through a $\frac{1}{8}$-in. plate and mixing thoroughly. Heat 5 g with a 20 per cent. soln. of trichloroacetic acid in 2 *M* H_3PO_4 (5 ml) and 0·01 *M* **I** (10 ml) for 30 min. on a bath of boiling water, chill in an ice bath for 10 min. and remove the solid fat layer. To the aq. layer add *iso*amyl alcohol (10 ml) and pyridine (5 ml), shake vigorously for 2 min., centrifuge at 2400 r.p.m. for 15 min., decant the clear extract into a 1-cm cell and measure the extinction at 538 mμ against a solvent blank.

A. R. ROGERS

548. **The detection of preservatives in processed cheese with the aid of paper chromatography. I. The detection of benzoic acid, *p*-chlorobenzoic acid and *p*-hydroxybenzoic acid and its salts and esters.** R. Jarczynski and F. Kiermeier (Chem. Phys. Inst. Süddeutsch., Weihenstephan, Germany (*Z. Lebensmittl Untersuch.*, 1954, **99** [2], 91–96).—*Procedure*—Reflux 40 g of cheese for 20 min. with 75 ml of 25 per cent. HCl. Cool, filter off the fat and extract with three 50-ml portions of ether - light petroleum mixture (1:1). Esters of *p*-hydroxybenzoic acid are partially hydrolysed by this procedure. Reflux the fat for 5 min. with 150 ml of H_2O made slightly alkaline with aq. NH_3 soln. Extract the aq. soln. as before and combine the extracts. Evaporate them and dissolve the residue in 2 to 4 ml of alcohol. Chromatograph with a solvent of butanol - conc. aq. NH_3 soln. - H_2O (70:20:10). Develop with a suitable indicator. Elute the benzoic and *p*-chlorobenzoic acids, if necessary, and confirm by Mohler's reaction. Then develop with diazotised sulphanilic acid to confirm *p*-hydroxybenzoic acid. Examine further under u.v. light for esters of *p*-hydroxybenzoic acid. W. H. PARR

549. **Determination of free galacturonic acid in citrus products.** V. V. Almendinger, C. A. Dillman and C. G. Beisel (Real Gold Citrus Products, Anaheim, California, U.S.A.) (*Food Tech., Champaign*, 1954, **8**, 86–88).—A method for determining free galacturonic acid in citrus fruit, juices and concentrates, based on the Tollens reaction with 1:3-dihydroxynaphthalene, is described. Results for 29 samples of orange and lemon products are reported. *Procedure*—Heat the sample (125 ml) at 85° C for 1 min., rapidly cool and dilute with acetone to 250 ml. Shake, allow the ppt. to settle, and filter through paper. Evaporate 200 ml of the filtrate to about 100 ml, decolorise at 80° C with activated carbon (1 g), cool and filter through a Büchner funnel, with Celite as filter aid. Pass the filtrate, followed by H_2O (250 ml), through cation- and anion-exchange resin columns (≃ 30 ml each of Duolite C–3 and A–4) at 7 to 8 ml per min. Backwash the anion column with H_2O (300 ml). Elute the acids with HCl (1 + 9) (75 ml) followed by H_2O (125 ml) at 8 to 10 ml per min. Discard the first 10 ml of eluate, and dilute the bulk to 200 ml. Shake a 1-ml aliquot with conc. HCl (2 ml) and 1 per cent. 1:3-dihydroxynaphthalene in 25 per cent. aq. acetone (2 ml) and heat at 50° ± 1° C for exactly 210 min. Cool to room temp., add ether (10 or 20 ml, according to the expected concn.) and shake for 5 to 7 min. After setting aside the soln. for 4 min., decant the ether layer, dry it with anhyd. Na_2SO_4 (0·5 g) for 2 min. and measure the extinction at 550 mμ. Prepare a blank by taking a 0·5 per cent. citric acid soln. through the steps following ion exchange. Calculate by means of a calibration curve. A. R. ROGERS

550. **Spectrophotometric analysis of the essential oils of citrus fruits.** R. Cultrera and E. Trifirò (*Chim. e Ind.*, 1955, **37** [9], 701–705).—Previous methods (Trifirò *et al.*, *Conserve e Deriv. Agrumari*, 1952, **1**, 2, 18; 1953, **2**, 77; 1954, **3**, 5) are further developed. Data are obtained and tabulated, making possible a rapid estimation of the purity of

an essential oil and showing the presence of adulterating matter. A series of transmission curves are illustrated for various types of essential oils.
C. A. FINCH

551. **Spectrophotometric determination of total methylxanthines content of refreshing beverages containing caffeine.** A. Schaller and H. Klaushofer (*Mitt. VersSta. Gärungsgew.*, 1955, **9** [7–8], 105–112).—A review is given of published data on the composition of these beverages, the alkaloid content of the ingredients kola-nut and maté-tea (chiefly caffeine and theobromine) and the spectrophotometric determination of these alkaloids. The values of $E_{1\,cm}^{0\cdot001\%}$ of caffeine and theobromine were determined in aq. soln. at 272 mμ as 0·05081 and 0·05512, respectively, and a method for their joint determination (as caffeine) is described. *Procedure*—The sample (50 ml), after having been shaken free from CO_2, if necessary, is first cleared by treatment with aq. 10 per cent. $CuSO_4.5H_2O$ (10 ml), aq. 5 per cent. NaOH (10 ml) and aq. 10 per cent. neutral Pb acetate (5 ml). The mixture is then made up to 100 ml and filtered; 50 ml of the clear filtrate are acidified with acetic acid and shaken out with four successive portions of 15 ml, followed by one of 10 ml of chloroform. The united chloroform extracts are dried (Na_2SO_4) and evaporated to dryness, after which the residue is dissolved in water, the soln. being made up to 250 ml for spectrophotometric measurement. The method is accurate within ± 1 per cent. Preliminary experiments on the determination of caffeine, theobromine and theophylline in maté-tea are described.
P. S. ARUP

552. **Determination of phenol in beer.** G. Gorbach, G. Dedic and O. G. Koch (*Fette u. Seifen*, 1955, **57** [6], 421–422).—To 250 ml of beer are added 10 ml of phosphate buffer soln. (pH 6·0) and steam is passed through the mixture until 250 ml of distillate have been collected. For beer containing 0·05 to 5 μg of phenol per ml, 50 ml of the distillate are mixed with 10 ml of borax buffer soln. (pH 9·4) and 0·5 ml of Gibbs' reagent (0·4 g of 2:6-dibromobenzoquinone-4-chlorimine in 100 ml of ethanol). The soln. is set aside in the dark for 1 hr. and the extinction is then measured at 590 mμ; a blank measurement is made at the same time and this is subtracted from the test reading. The phenol content is determined by means of a calibration curve. For samples containing 0·001 to 0·1 μg of phenol, the reaction mixture is extracted with *n*-butanol and the extinction of the extract is measured at 610 mμ.
E. HAYES

553. **A colour reaction of fermented products.** L. Rosenthaler and G. Vegezzi (*Z. Lebensmitt-Untersuch.*, 1955, **102** [1], 33–34).—A red coloration due to a hitherto unidentified constituent (probably containing a CO group) has been obtained on adding to fermented products or their distillates (2·5 ml), ethanolic 50 per cent. hexylresorcinol (2 drops) and conc. trichloroacetic acid (2·5 ml). Positive results were obtained with 200 samples of acraldehyde-free brandy of various descriptions, or with their distillates. In some instances the coloration could be obtained only with the last fraction or from the residue of a distillation of the sample; it was generally obtained within 2 hr. after mixing, but sometimes not until after 5 hr. In the presence of acraldehyde, and with the further addition to the reaction mixture of $HgCl_2$, the mixed coloration resembles that of dil. aq. $KMnO_4$. The red coloration is more permanent than that due to the acraldehyde reaction.
P. S. ARUP

554. **The detection of cinnamaldehyde in dessert wines and wine-containing liquors, by paper chromatography.** H. Grohmann and F. H. Mühlberger (*Z. LebensmittUntersuch.*, 1954, **99** [6], 361–367).—Cinnamaldehyde (**I**) can be differentiated from vanillin by the colours produced with hydrazine and benzidine. Oxidation of the aldehyde on paper is reduced to a minimum by a rapid method. *Procedure*—Acidify 100 ml of wine with 5 ml of 20 per cent. phosphoric acid and shake the soln. for 15 min. with 50 ml of pentane in a separating funnel. Centrifuge, and evaporate the soln. and dissolve the residue in 1 ml of ethanol. Chromatograph for 30 min., with water-satd. light petroleum (boiling range 120° to 180° C). Dry in air and develop with hydrazine reagent (10 ml of 25 per cent. HCl and 90 ml of satd. aqueous hydrazine sulphate). With an R_F of 0·82, **I** gives a citron-yellow colour in daylight, pale yellow in u.v. light; vanillin gives a deeper yellow colour. The sensitivity is 2 μg in daylight, 1 μg in u.v. light. Confirm by spraying a duplicate chromatogram with benzidine (0·5 g in 20 ml of acetic acid and 80 ml of alcohol). The colours produced by **I** and vanillin in daylight are dark brown and orange - red, respectively. Tests show that **I** does not occur naturally in wine.
W. H. PARR

555. **Determination of citric acid in wine.** K. Täufel and R. Pohloudek-Fabini (*Z. Lebensmitt-Untersuch.*, 1955, **102** [1], 28–32).—Descriptions are given of two adaptations of the pentabromoacetone (**I**) method. In the first method the diluted sample is acidified with H_2SO_4 and boiled for 10 min., after which the citric acid is converted into **I** by the usual method. In the second method the citric acid is separated as the insol. bismuth salt, and liberated by acidification with phosphoric and acetic acids for conversion into **I**. In both methods **I** is quant. extracted by means of light petroleum, and determined colorimetrically by its reaction with Na_2S, comparison being made in aq. 50 per cent. pyridine soln. with results obtained with standard soln. of citric acid. Both methods show good reproducibility; they are accurate within ± 5 per cent. and compare favourably with Reichard's original gravimetric method. Comparative results for a number of different wines show that the second of the above methods need only be employed for sweet wines.
P. S. ARUP

556. **Spectrophotometric determination of the natural colouring material in distilled spirits.** R. L. Schoeneman, M. J. Pro and A. P. Mathers (Alcohol and Tobacco Tax Div. Lab., Int. Rev. Service, Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [3], 821–825).—The colouring matter in whisky which is derived from the wooden containers in which it is aged is determined spectrophotometrically. Whisky (20 ml) is treated, successively, with 10 ml of saturated NaCl solution, 0·5 ml of conc. HCl, and 10 ml of methyl propyl ketone. After 10 to 15 inversions of the vessel, the layers are allowed to separate, the volume of the solvent layer is read, and its absorbance at 430 mμ is determined. A table gives representative values, in colour units, for total and organic soluble colour in various samples. For straight whisky the ratio of organic-soluble colour to total colour is approximately 0·9:1.
A. A. ELDRIDGE

557. **Isolation and separation of coal-tar colours in foods.** C. Graichen, R. N. Sclar, N. Ettelstein and K. A. Freeman (Food and Drug Admin., Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [3], 792–796).—By means of the procedure described, acid coal-tar colours can be separated by column chromatography on powdered cellulose (*e.g.*, Solka-Floc BW–40) in amounts suitable for spectrophotometric identification. The technique for extraction by means of water, light petroleum, ether or 80 per cent. alcohol is detailed. Unless considerable decomposition occurs during isolation of the colour, the method can be applied quantitatively. A. A. ELDRIDGE

558. **Separation of fatty acids through urea-adduct formation and amide crystallisation.** K. T. Achaya, B. P. Baliga, S. A. Saletore and S. H. Zaheer (*J. Sci. Ind. Res., B, India*, 1955, **14** [7], 348–354).—The resolution of mixed fatty acids from groundnut, safflower seed, cottonseed, linseed, castor, and dehydrated castor oils through urea-adduct formation, by using solutions of urea in methanol or ethanol, solid urea, and aqueous solutions of urea, has been investigated. Several variations of these separation procedures are also reported. Resolutions employing methanol - urea were the most selective, especially with unsaturated acids. Ethanol (80 per cent.) - urea results were broadly similar to those obtained with methanol, but a loss in selectivity was observed with higher unsaturated fatty acids in the final fractions. Solid urea was intermediate between the two. Under certain conditions aq. urea soln. gave results similar to those from ethanol - urea. Separation of methyl esters of unsaturated linseed-oil fatty acids, a ricinoleic - linoleic - oleic acid mixture, and an oleic - linoleic acid mixture was also carried out. The results show that adduct formation is not sufficiently selective for resolution of refractory acid mixtures in the form of esters. Fractionation of fatty-acid amides by crystallisation from acetone and alcohol was less efficient than urea-adduct formation and the conventional lead-salt and low-temp. crystallisation methods. G. C. JONES

559. **The spectrophotometric determination of polyethylenic acids [in fats].** J. Moretti and R. I. Cheftel (Lab. Biochem., 45 rue des Saints-Pères, Paris) (*Bull. Soc. Chim. Biol.*, 1955, **37** [5–6], 699–707).—The development of the method of determining the double bonds in fats by u.v. spectrophotometry is reviewed and the influence of various factors is studied. A working procedure is described and the importance of strict attention to detail in order to obtain reproducible results is emphasised. H. F. W. KIRKPATRICK

560. **Filter-paper test for the detection of peroxide compounds.** K. Täufel and R. Vogel (*Fette u. Seifen*, 1955, **57** [6], 393–399).—By means of a micro-pipette, 0·025 ml of a 5 per cent. soln. of an oil or fat in anhydrous acetone is dropped on filter-paper (Whatman No. 1 or Schleicher and Schüll 2043a or 2043b) and the spot is sprayed with a soln. of $FeSO_4$ containing NH_4SCN. The colour developed is compared with similar colours produced by oils of known peroxide value; a permanent photographic comparison scale can also be used. Peroxide values (ml of 0·002 *N* $Na_2S_2O_3$ per g of fat) from 7·5 to 150 can be differentiated readily. For the preparation of the $FeSO_4$ - NH_4SCN reagent, 5 g of $FeSO_4.7H_2O$ are dissolved in 50 ml of a 10 per cent. aq. soln. of NH_4SCN containing 0·5 ml of conc. H_2SO_4; 0·3 g of iron powder is added and the container is stoppered with a Bunsen valve. Five ml of this conc. soln., which is stable for a month, are mixed with 45 ml of a mixture of equal vol. of freshly boiled water and freshly distilled acetone. By measuring the peroxide value developed after the paper has been exposed to the air for a definite time, the resistance to autoxidation of different oils can be compared. A paper-chromatographic method for carrying out the Kreis test for aldehydes is also described. E. HAYES

561. **Antioxidants and their detection.** H. Janecke (Univ.-Inst. Lebensmittelchemie, Frankfurt, Germany) (*Dtsch. LebensmittRdsch.*, 1955, **51** [5], 121–124).—A review is given of the properties and methods of detection of antioxidants commonly present in foodstuffs. Methyl, ethyl and propyl gallates are soluble in water, the higher gallates in warm 72 per cent. ethanol, 2:3-di-(3:4-dihydroxybenzyl)butane (nordihydroguaiaretic acid) (**I**) and *tert.*-butyl-4-hydroxyanisole (BHA) in cold 72 per cent. ethanol, and the tocopherols in absolute ethanol. The gallates give a rose colour with aq. NH_3 soln. With Gibbs' reagent (borax and 2:6-dibromobenzoquinone-4-chlorimine), **I** and BHA give blue colours, the latter fluorescing blue in u.v. light; **I** and the gallates give a blue colour with $Ba(OH)_2$ and rose with NaOH. All these antioxidants give a positive reaction (red colour) with $FeCl_3$ and 2:2′-dipyridyl. A. R. ROGERS

562. **Paper-chromatographic detection of anti-oxidants.** K. F. Gander (*Fette u. Seifen*, 1955, **57** [6], 423–425).—Methods for the separation and detection of 11 common antioxidants are described. An ascending technique with Whatman No. 1 or S & S 2043b paper is used. R_F values are given for the following solvents: (*i*) methanol - *iso*amyl alcohol - benzene - water (2:1:1:1), (*ii*) water - ethyl acetate (97·5:2·5), (*iii*) methanol, (*iv*) *n*-butanol - acetic acid - water (4:1:5). The spots are developed by spraying with (*a*) a 1 per cent. soln. of $AgNO_3$ followed by a 1 per cent. aq. NH_3 soln. or (*b*) a 2 per cent. borax soln. followed by a 0·01 per cent. ethanolic soln. of 2:6-dichlorobenzoquinone-4-chlorimine. Reagent (*b*) is especially suitable for the detection of butylated hydroxyanisole (*tert.*-butyl-4-hydroxyanisole) and tetramethylthiuram disulphide, but it is less sensitive than (*a*). For the detection of antioxidants in lard or margarine, a 40-g sample is dissolved in light petroleum (boiling range 42° to 68° C) and the soln. is shaken with 96 per cent. ethanol. The 3 to 4-ml ethanolic layer that forms is separated and five 0·02-ml drops are placed on the paper, the solvent being allowed to dry off after each addition. The chromatogram is then developed with one of the solvents described. E. HAYES

563. **Quantitative determination of vitamins in pharmaceutical mixtures.** G. A. Vaisman and S. G. Rozhntskaya (*Aptechnoe Delo*, 1955, **4** [3], 16–20).—Simple methods of determining ascorbic acid, thiamine and nicotinic acid are applied to mixtures containing these vitamins with various pharmaceutical preparations. Ascorbic acid can be determined iodimetrically in the presence of Ca lactate, phytin, glucose, Ca glycerophosphate, caffeine Na benzoate, nicotinic acid, amidopyrine or thiamine. For mixtures containing ascorbic acid and nicotinic acid, the ascorbic acid is determined iodimetrically and the total acid is then titrated against 0·1 *N*

soln. of HCl, with phenol red as indicator. Thiamine is determined in the presence of ascorbic acid by a modification of the U.S.S.R. Pharmacopoeia VIII argentimetric method. E. HAYES

564. **Use of activated glycerol dichlorohydrin for estimating vitamin A in dairy-calf blood plasma.** R. S. Allen, P. G. Homeyer and N. L. Jacobson (*Iowa St. Coll. J. Sci.*, 1955, **29** [4], 721–734).—It is reported that reagents containing < 0·025 per cent. of $SbCl_3$ and having an HCl concn. of < 0·01 *N* are not entirely satisfactory, even when the saponification procedure is employed. Repeated distillation of glycerol dichlorohydrin reduces both free HCl and the content of $SbCl_3$ and renders the reagent unsatisfactory. E. G. BRICKELL

565. **The colorimetric determination of calciferol.** J. Büchi and H. Schneider (Pharm. Inst., Eidg. Techn. Hochschule, Zürich, Switzerland) (*Medd. Norsk Farm. Selsk.*, 1955, **17** [4–5], 87–115).—The method of Schaltegger (*Brit. Abstr. C*, 1946, 186) for the colorimetric determination of calciferol (**I**) has been critically examined, and modifications are suggested to improve the assay of **I** and of conc. oily soln. of **I**. *Procedure*—To a soln. of the sample (≃ 100 μg of **I**) in thiophen-free benzene (1 ml) add 2 ml of a freshly prepared soln. of 0·15 per cent. 4-*iso*propylbenzaldehyde in thiophen-free benzene. Dilute with thiophen-free benzene (4 ml) and add perchloric acid reagent (**II**) (3 drops). Reflux on a bath of boiling water for 1·5 min. in the dark, allow to stand for 7 min. in the dark while cooling, add acetic acid (3 ml) and compare the extinction at 550 mμ with that of water, the measurement being made 9 min. after the heating. **II** is prepared by heating a mixture of acetic anhydride (2 ml), acetic acid (2·5 ml) and 60 per cent. perchloric acid (0·6 ml) for 30 min. at 95° to 100° C, the access of moisture being prevented. A. R. ROGERS

566. **Determination of nicotinamide and nicotinic acid. I. Nicotinamide.** A. Barreto, F. A. Gai and H. S. R. Barreto (*Rev. Quím. Ind., Rio de Janeiro*, 1955, **24**, 12).—Chloranilic acid forms coloured precipitates with nicotinamide and nicotinic acid, that from nicotinamide being produced first. The compound from nicotinamide is a well-crystallised red solid, soluble in water, sparingly soluble in ethanol and insoluble in amyl acetate and ether. It sublimes at 180° C and decomposes at 240° to 245° C; an aqueous solution has a pH of 3 at 23° C and a conductivity of 6·0 × 10^{-4} mho × cm^{-1}. The reaction was used for the determination of the vitamin either gravimetrically or colorimetrically. *Gravimetric method*—An aliquot containing 0·01 to 0·1 g of nicotinamide in amyl acetate or ether is mixed with an excess of chloranilic acid solution (0·025 *M* in amyl acetate or ether). The mixture is allowed to stand for 30 min. in amyl acetate or 5 min. in ether, then filtered through a weighed Gooch crucible. The ppt. is washed with chloranilic acid solution, and then with ether until the ether washings give no colour when mixed with water. The ppt. is dried to constant weight and the nicotinamide is calculated. *Colorimetric method*—The ppt. is dissolved in water and the colour intensity is measured. Interfering substances can readily be removed by filtration. H. PRITCHARD

567. **Identification of vitamin C by paper chromatography of the dinitrophenylhydrazones.** R. C. R. Barreto (*Rev. Quím. Ind., Rio de Janeiro*, 1955, **24**, 13).—During the examination of vegetable infusions for the presence of vitamin C, the ascending - descending paper-chromatographic method of Block was used on the dinitrosazones. Many combinations of solvent were used, but a mixture of *iso*butanol and aq. 5 per cent. NH_3 (90:10) and a mixture of xylene and nitrobenzene (95:5) were the most satisfactory. Of these, the latter solvent furnished compact spots of such definition that treatment with alcoholic potash to reveal them was unnecessary. H. PRITCHARD

568. **A method for recovery of extraneous material in ground cinnamon.** G. Schwartzman (Food and Drug Admin., Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [3], 781–782).—The sample, which may be contained in a bolting-cloth bag, is steeped in light-petroleum at 100° C for 30 min. The light-petroleum layer is decanted and a mixture (1:1) of $CHCl_3$ and CCl_4 is added. After 1 hr., this is decanted through filter-paper on a Büchner funnel and the sample is dried. It is then stirred with aqueous alcoholic Na oxalate soln., and treated with an aqueous alcoholic soln. of EDTA (tetrasodium salt) followed by petrol. After 1·5 hr., the particles thus flocculated are filtered off and, after repetition of the treatment, are examined microscopically for rodent hair and insect fragments. A. A. ELDRIDGE

569. **Identification of rodent-fur hairs.** D. B. Scott (Food and Drug Admin., Dept. Health, Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [2], 503–506).—The fur hairs of the rat, mouse, rabbit, squirrel and musk-rat were mounted in glycerin jelly and examined microscopically without further treatment. The structure of the medullary segment and adjacent air vesicle is characteristic. The fur hairs of the mouse and rat are very similar. Photographs are reproduced. A. A. ELDRIDGE

See also Abstracts 459, 482, 484.

Sanitation

570. **Chemical analyses with an ultra-violet filter photometer. I. Determination of a small amount of sulphate in water.** Takeshi Kato, Yasuaki Nomizo and Koichiro Shinra (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [4], 373–376).—The light extinction of CrO_4'' in an ammoniacal soln. at 405 and 366 mμ conforms to Beer's law when a filter photometer, which makes use of the spectral lines of Hg (405 mμ and 366 mμ), is employed as the light source. Sulphate ions react with $BaCrO_4$ in an acidic soln. to give $BaSO_4$ and Cr_2O_7''. The sample (2 to 120 μg of SO_4'' per ml) (50 ml) is made slightly acid with 4 *N* acetic acid (2 ml) and *M* Na acetate (2 ml), then treated with $BaCrO_4$ (20 g in 1 litre of 5 per cent. $HClO_4$) (3 ml), with vigorous shaking (pH of the soln., 1·1 to 1·4). The product is made alkaline with 4 *N* aq. NH_3 soln., diluted with water and filtered. The extinction of the filtrate is measured at 366 mμ (for 2 to 17 μg of SO_4'' per ml) or at 405 mμ (10 to 120 μg per ml), and the amount of sulphate is calculated. The presence of Fe^{++}, SO_3'', PO_4''' and a large amount of Mn interferes with the result. This method appears to be suitable for the determination of SO_4'' in natural and polluted water. K. SAITO

571. **Colorimetric determination of nitrate ions. II. A new method with aniline for nitrate in water.** Takio Kato, Yutaka Okinaka and Keiichi Sakai (*Japan Analyst*, 1954, **3** [3], 231–236).—The use of aniline (acetate) in place of sulphanilic acid for the colorimetric determination of nitrate in the presence of nitrite is suggested. Nitrite ($< 1{\cdot}5$ μg per ml) can be completely decomposed by boiling with aniline acetate in an acidic soln. (pH $\simeq$ 4). Nitrate is reduced to NO_2' with zinc dust at pH 5·2, then coupled with 1-naphthylamine at pH 3·0. The sample (30 ml) is heated almost to boiling point with aniline acetate soln. (3 ml of aniline and 3 ml of glacial acetic acid per 100 ml of water) (2 ml), then cooled to below 15° C and treated with Na acetate (1 g) and zinc dust (2 g) for 10 min., with vigorous shaking. The product is filtered, made acid with a mixture of 6 *N* HCl and glacial acetic acid (1:1) (2 ml), and treated with 1-naphthylamine (1 g per 50 ml of water containing 14·5 ml of glacial acetic acid) (1 ml); the extinction is measured at 530 mμ. The pink soln. conforms to Beer's law for up to 2·0 μg of NO_3' per ml. Interference results from the presence of sulphide, SO_3'' (> 10 μg per ml) and Cu (> 5 μg), but not from that of NaCl (< 3 per cent.), Fe''' (< 50 μg per ml), Ca'', Mg'', Mn'' and Fe''. This method appears to be especially suitable for the determination of NO_3' in natural water, including sea water.
K. Saito

572. **Colorimetric determination of low concentrations of dissolved oxygen in water.** L. S. Buchoff, N. M. Ingber and J. H. Brady (U.S.N. Engng Exp. Station, Annapolis, Md., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1401–1404).—Oxygen (up to 50 parts per thousand million) is determined by measurement of the colour intensity of a soln. containing reduced indigo carmine. Comparison is made by eye or at 555 mμ against artificial standards.
D. A. Pantony

573. **The determination of traces of benzene hexachloride in water and sewage effluents.** W. Hancock and E. Q. Laws (Government Laboratory, Clement's Inn Passage, London) (*Analyst*, 1955, **80**, 665–673).—The hexachloro*cyclo*hexane (benzene hexachloride) is removed from aq. soln. by adsorption on charcoal in a chromatographic apparatus that permits of the transference of the charcoal column into a flask fitted with a reflux water condenser, from the upper end of which glass tubing terminating in a sintered-glass disc leads into a nitrating mixture of HNO_3 and H_2SO_4. The charcoal is treated with an acetic acid - acetic anhydride mixture, zinc dust and malonic acid, and the apparatus is heated so that the acetic acid refluxes gently for 1 hr. The CO_2 formed by decomposition of the malonic acid provides a gas stream to sweep out all the benzene into the nitrating acid. The *m*-dinitrobenzene so formed is extracted from the diluted acid with ether and, after removal of the ether, is mechanically shaken with butanone and aq. KOH soln. for 45 min. The optical density of the butanone layer, separated by centrifuging, is measured at 565 mμ or in a Spekker absorptiometer with a No. 6 filter. The original concn. of hexachloro*cyclo*hexane is ascertained from a calibration graph prepared by submitting known amounts of γ-hexachloro*cyclo*hexane to the dechlorinating and nitrating reaction in the presence of charcoal. The determination can also be made colorimetrically by visual comparison with an alcoholic soln. of alizarin. The possibility of concentrating the material from very large volumes is demonstrated.
A. O. Jones

574. **Analyses of sewage and trade effluents.** H. B. Tench (*J. Inst. Sewage Purif.*, 1954, [2], 140–148).—Current methods of analysis or testing of the following are reviewed and discussed: ammoniacal, nitrous and nitric nitrogen, Cl, albuminoid nitrogen, 3-min. oxygen absorption from $KMnO_4$, 4-hr. oxygen absorption from $KMnO_4$, 5-day B.O.D., suspended solids and stability; and, for trade wastes, alkalinity, sulphates, sulphides, cyanide and Cr.
S.C.I. Abstr.

575. **The detection and determination of traces of polynuclear hydrocarbons in industrial effluents and sewage. III. The examination of some gasworks effluents.** P. Wedgwood and R. L. Cooper (Eastern Gas Board, Clarendon Road, Watford, England) (*Analyst*, 1955, **80**, 652–654).—The source of the small amounts of polynuclear aromatic hydrocarbons in sewage has been traced in part to gasworks wastes and, in particular, to the aq. effluent from carburetted water-gas plant. The method used consists essentially in extraction of the hydrocarbons with chloroform, transference to *cyclo*hexane, chromatographic fractionation and spectrophotometric examination of the fractions. Spent ammoniacal liquor is shown to contain pyrene, an alkylpyrene, fluoranthene, 1:2-benzanthracene, chrysene, perylene, 1:2-benzopyrene, 3:4-benzopyrene, anthanthrene, and possibly triphenylene. Many of these occur in higher amounts in the solid deposit from the liquor. De-oiled effluent from carburetted water-gas plant is richer in hydrocarbons than the spent liquor and the following were found or suspected—naphthalene, acenaphthylene, phenanthrene, fluorene, anthracene, pyrene, fluoranthene, perylene, 1:2-benzopyrene, 3:4-benzopyrene, anthanthrene and 1:12-benzoperylene. Much smaller amounts of such hydrocarbons are derived from atmospheric pollution during rain or snowfalls.
A. O. Jones

576. **Modification of the ferrous thiocyanate colorimetric method for the determination of some atmospheric oxidants.** G. W. Todd (Univ. California, Riverside, Calif., U.S.A.) (*Anal. Chem.*, 1955, **27** [9], 1490–1492).—Oxidising gases, especially those from treatment of olefins with ozone, are determined by the intensity of the $Fe(SCN)_3$ colour produced in a $Fe(SCN)_2$ reagent.
D. A. Pantony

577. **Improved apparatus and procedures for sampling and analysing air for fluorides.** R. Mavrodineanu and R. R. Coe (*Contr. Boyce Thompson Inst.*, 1955, **18** [3], 173–180).—Apparatus and procedures are described for sampling and analysing air contaminated with SiF_4 and HF at concn. from one to several hundred pt. per 10^9. The air is drawn into a conical absorber, containing 50 ml of F-free water, at 10 to 84 cu. ft. per hr., when a 95 per cent. recovery is made. A smaller absorber containing 40 ml of absorbing liquid is equally efficient for air speeds of 40 cu. ft. per hr.; on subsequent distillation a recovery of F of 95 per cent. is given, with an average blank of 1 μg. An automatic time-clock sampler is also described. Suitable aliquots of the soln. containing F are made up in polyethylene apparatus and, after the pH has been adjusted to 3·0 $\pm$ 0·05 with 0·1 *N* NaOH and 0·1 *N* HCl, are placed in Nessler tubes with

2 ml of a 0·01 per cent. soln. of Na alizarinsulphonate and made up to the required volume with water of pH 3·0. Thorium nitrate soln. (2 g per litre) is then added until a suitable pink colour is obtained; blanks containing NaF are similarly treated for evaluating the unknown soln. With soln. containing > 10 μg of F per 100 ml the addition of 80 per cent. of the estimated NaF required is added before the addition of the thorium nitrate. G. R. WHALLEY

578. **The chromatographic identification and estimation of the active ingredients in pyrethrum extracts.** C. Bergamini and W. Versorese (*Sperimentale*, 1954, **5** [1–2], 6–10).—A method for the separation of pyrethrins I and II in pyrethrum extracts by circular chromatography is described. An advantage of the method is that the alkaline hydrolysis liquor may be used without further purification, on addition of an equal vol. of alcohol. Pyrethrin I is more mobile and yields, on development with Denigès's reagent, a pink band which rapidly changes to red, purple and brown. Pyrethrin II yields a distinct yellow band on being heated to 70° C for 7 to 10 min., which is stable for 1 hr. The sensitivity is $\simeq 30$ μg. The method can be made quantitative for pyrethrin II by measurement of the total optical density. The R_F values of the pyrethrins in various solvents are given, and a typical chromatogram is reproduced in colour. H. A. FISHER

579. **Detection of DDT.** L. Garbe and G. Krippner (*Chem. Tech., Berlin*, 1955, **7** [7], 424).—A rapid and reliable method for detecting DDT consists in dissolving or suspending a small sample in 0·5 ml of acetone, mixing the resulting suspension or solution with 1 to 2 drops of 0·5 *N* alcoholic KOH, evaporating off the solvent, and spotting with a solution of 0·25 g of $K_2Cr_2O_7$ in 100 ml of conc. H_2SO_4. The presence of DDT is shown by a carmine-red coloration. When a small amount (a μg quantity) of DDT is present it is necessary, to avoid the colour of the solution masking the colour change, to use a 1:15 mixture of dichromate and H_2SO_4, which must be freshly prepared. For very low amounts ($<$ μg quantities) of DDT it is advisable to evaporate off the solvent at low (room) temp. Instead of the dichromate - H_2SO_4 solution, 45 per cent. oleum can be used. The colorations produced are not very lasting. The identification is possible in the presence of hexachloro*cyclo*hexane. When the sample contains liquid products it is first highly diluted with acetone, and a few drops of this solution are used for the test; 1 μg of DDT can be detected. The known reaction between DDT and dichromate - H_2SO_4 in combination with certain solvents such as ether or acetone to give a pale carmine colour is not as sensitive as the test described and is not specific for DDT. H. L. WHITEHEAD

Agriculture and Plant Biochemistry

580. **Colorimetric determination of biuret.** G. C. Ellis and R. L. Formaini (Allied Chem. and Dye Corp., Hopewell, Va., U.S.A.) (*J. Agric. Food Chem.*, 1955, **3** [7], 615–618).—In developing this method for determination of biuret in urea pyrolysates, consideration was given to water solubility of urea pyrolysate, biuret concn. and acceptable colorimetric scale limits. For samples sol. in water at 25° C, a weighed pulverised sample containing 0·4 to 1·8 g of biuret is dissolved in 500 ml of water, neutralised to pH 7·0, transferred to a 1-litre flask and made up to the mark. A 50-ml aliquot of the soln. is transferred to a 100-ml flask, 20 ml of alkaline tartrate and 20 ml of $CuSO_4$ reagent soln. are added, and the solution is made up to the mark. The flask is suspended in a thermostat for 15 to 30 min. The colorimetric scale reading is determined with a photo-electric colorimeter, No. 54 green filter (spectral range 490 to 570 mμ). For samples insoluble in water at 25° C, the weighed sample containing 0·4 to 1·2 g of biuret is placed in a 1-litre beaker, 700 ml of water are added and the suspension is heated to 70° or 80° C, cooled to 30° C, neutralised to pH 7·0 and filtered into a 1-litre flask. The residue is washed with three 50-ml portions of water, the washings are added to the filtrate and the solution is made up to the mark. A 50-ml aliquot is transferred to a 100-ml flask and the copper biuret complex is formed as above. A standard curve is prepared. The method is quick and accurate to within $\pm$ 0·5 per cent., provided that measurements are made in the linear portion of the standard curve, and interfering materials are maintained within acceptable limits. S.C.I. ABSTR.

581. **The determination of the N-terminal amino-acids of some prolamines.** T. Deutsch (Magyar Tudományos Akad. Biokém. Intézete) (*Magyar Kém. Foly.*, 1955, **61** [5], 135–137).—Sanger's 1-fluoro-2:4-dinitrobenzene method was used, as described earlier (Deutsch, *Acta Physiol. Hung.*, 1954, **6**, 209) for the determination of the N-terminal amino-acid in some plant proteins; the amino acids thus obtained were identified by paper chromatography in 1 *M* Na citrate (pH 6·4) and in *iso*-butanol - butyl acetate - 2 per cent. HCl (5:3:2, by vol.). A. G. PETO

582. **Routine determination of the base-exchange capacity and of the exchangeable bases in soil analysis.** S. Cecconi and A. Polesello (Univ. Florence, Italy) (*Ann. Sper. Agr.*, 1954, **8**, 1459–1470).—A simplified procedure for the determination of the total base-exchange capacity and for the quant. determination of exchangeable $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$ and $K^{\cdot}$ is described, and a modification to adapt the method to soils with a high content of $CaCO_3$ is given. *Procedure*—Place the samples of fine dry soil on washed moist filter-papers contained in glass funnels with stems closed by means of rubber tubing and clips. Cover the samples overnight with *N* ammonium acetate soln. (pH 7). Filter the soln. and wash with ammonium acetate soln. till 250 ml of filtrate (**I**) have been collected. Use **I** for the determination of total exchangeable bases and for exchangeable Ca and Mg. In soils with high content of $CaCO_3$ use the filtrate **I** for the determination of $K^{\cdot}$ only. For the determination of $NH_4^{\cdot}$ displaced by $Ba^{\cdot\cdot}$, place 5 ml of *N* NH_4Cl on each filter, allow the soln. to drain through, discard the rubber tube and wash the filter with 80 per cent. alcohol containing 1 drop of conc. aq. NH_3 soln. per litre till the filtrate is free from Cl'. Finally, wash the filter with 0·5 *N* $BaCl_2$ till $NH_4^{\cdot}$ are absent. To the filtrate add 5 ml of 40 per cent. formaldehyde and titrate with 0·05 *N* $Ba(OH)_2$ to phenolphthalein to a standard colour. Careful tests show that added $CaCO_3$ (40 per cent.) does not

materially affect the result. The titration of the total exchangeable bases, and of $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$ and $K^{\cdot}$ in **I** is described in detail. The method is claimed to be rapid and accurate. H. A. FISHER

583. **Photocolorimetric method of determining fluorine in fertilisers.** K. Lasiewicz (*Przem. Chem.*, 1954, **10**, 36–38).—Gravimetric methods of Fresenius and of Willard are long and not very accurate (3 per cent. error). Colorimetric methods (error 1·5 per cent.) depend on the ability of fluorine to form stable colourless complexes with Ti, Zr, Mn and Fe and so reduce the colour intensity of the systems Ti - H_2O_2, Fe - SCN′, etc. The first of these has been investigated. To avoid colour effects from impurities, the fluorine is converted into Na_2SiF_6. Standard solutions of H_2SO_4, H_2O_2, Na_2SiF_6 and titanium are prepared to give standard colours, and extinctions are measured in a Pulfrich photometer, with violet filter S42, at 420 mμ. As extinction increases with temp., measurements were made at 20° C. Time, H_2O_2 (even a sixfold excess) and H_2SO_4 (small quantities) have no effect.
A. O. JAKUBOVIC

584. **The analysis of cyanogen compounds. I. A direct determination of cyanamide.** Shinsuke Takei (*Japan Analyst*, 1954, **3** [3], 243–246).—A direct volumetric analysis of cyanamide was studied with malachite green as indicator. Calcium cyanamide (8 g) is extracted with water and made up to 1 litre. A 25-ml portion is made acid with dil. HNO_3, treated with acetone (20 ml) and 0·25 *N* aq. NH_3 soln. (1·0 ml) and titrated with 0·1 *N* $AgNO_3$, malachite green (0·5 per cent.) (3 drops) being used as indicator. When the titration is carried out in the absence of aq. NH_3, the values obtained are too high because of the slow response of the indicator, but $NH_4^{\cdot}$ interfere with the result to a marked extent. This effect can be masked by the addition of NaOH. No interference results from the presence of guanidine, dicyandiamide and urea. The average deviation from the result obtained by the standard method is $<$ 1 per cent. **II. A rapid extraction of cyanamide from calcium cyanamide.** Shinsuke Takei (*Ibid.*, 1954, **3** [5], 415–416).—In an attempt to decrease the time occupied by the extraction of cyanamide from commercial "lime nitrogen," the use of dil. acetic acid was examined. Cyanamide is very stable in *N* acetic acid at $<$ 15° C, and its extraction from a sample (−200 mesh, 2 g) with 0·1 *N* acetic acid (450 ml) is completed within 30 min. The product is neutralised with 20 per cent. NaOH (phenolphthalein) (not with aq. NH_3 soln.), made acid with dil. HNO_3 and treated with an ammoniacal soln. of $AgNO_3$ to ppt. AgCN, which is dissolved in *N* HNO_3 and titrated with KSCN by the usual method. (See also Takei and Kato, *Technol. Rep. Tôhoku Univ.*, 1955, **19** [2], 167.)
K. SAITO

585. **A new method for the determination of calcium cyanamide in commercial "lime nitrogen."** Makoto Sato, Makoto Sato, Tadashi Fujisawa and Seiichi Sato (*J. Electrochem. Soc. Japan*, 1955, **23** [5], 238–241).—Direct potentiometric titration of calcium cyanamide with $AgNO_3$ provides satisfactory results for industrial analysis. The method is subject to interference by free CaO, which is often found in commercial "lime nitrogen," but this effect can be eliminated by the addition of a small amount of ammonium oxalate. The sample (0·25 g) is extracted by shaking with water (500 ml) for 10 min. A 10-ml portion is treated with 1 per cent. ammonium oxalate (50 ml) and titrated potentiometrically with a standard soln. of $Ag^{\cdot}$. The interference of sulphide (not usually present in the sample) can be eliminated by the addition of Cd acetate.
K. SAITO

586. **An improved method for the direct titration of phosphorus pentoxide in high analysis phosphatic materials.** P. McG. Shuey (Shuey and Co., Savannah, Ga., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [3], 761–763).—After the ammonium molybdophosphate [obtained by the method described in Methods of Analysis, 2.11–2.13 (*a*)] has been dissolved in 0·3662 *N* NaOH (1 ml ≡ 1 mg of P_2O_5), neutralised formaldehyde - phenolphthalein solution (1 ml in excess of 10 per cent. of the no. of mg of P_2O_5 being titrated) is added, and the solution is titrated to the first end-point change.
A. A. ELDRIDGE

587. **A rapid potentiometric method for the determination of soluble chlorine in feeds.** C. A. Luhman (Calif. Dept. of Agric., Sacramento, Calif., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [3], 764–766).—The sample is treated with 250 ml of water and 1 ml of conc. HNO_3; after 10 min. it is titrated potentiometrically with $AgNO_3$ soln. For practical purposes the voltage end-point obtained from one sample may serve as the end-point potential for all samples in the same series. For NaCl added to typical feeds, recoveries of 99·5 to 101·3 per cent. are reported. A. A. ELDRIDGE

588. **Paper chromatography of some organic phosphate insecticides. V. Conversion of organic phosphates to *in vitro* cholinesterase inhibitors by N-bromosuccinimide and ultra-violet light.** J. W. Cook (Food and Drug Admin., Washington, D.C., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [3], 826–832).—Photographs of paper chromatograms of various organic phosphate insecticides, prepared by the technique described earlier (*Ibid.*, 1955, **38** [1], 150), illustrate that by treatment with N-bromosuccinimide and ultra-violet light the insecticides afford products of greater potency in cholinesterase inhibition. The wavelengths of greatest activity are probably in the range 300 to 400 mμ. The compounds formed are more soluble in water than in oil.
A. A. ELDRIDGE

589. **Colorimetric analysis of *p*-chlorobenzyl *p*-chlorophenyl sulphide (chlorbenside) residues in plant and animal tissues.** D. J. Higgons and D. W. Kilbey (Boots Pure Drug Co. Ltd., Nottingham, England) (*J. Sci. Food Agric.*, 1955, **6** [8], 441–448).—The method is based on the pre-oxidation of spray deposits of chlorbenside to the corresponding sulphone with H_2O_2 in glacial acetic acid, and nitration of the sulphone to its corresponding trinitro derivative, which in benzene develops a purple colour with Na methoxide. The colour, which is not stable, reaches a reproducible peak 1 to 2 min. after development. The method is sensitive to 0·05 mg and is specific in the presence of normal impurities and other spray materials, except DDT.
S.C.I. ABSTR.

590. **Spray application problems. XIII. Determination of Captan deposits: progress report.** J. T. Martin and J. A. Pickard (*Ann. Rep. Agric. Hort.*

Res. Sta., Bristol, 1954, 83–89).—A method of determining the amount of deposited Captan (N-trichloromethylthio-4-*cyclo*hexene-1:2-dicarboxyimide) on fruits is described. The fruit (≃ 100 g) is washed with successive amounts of warm $CHCl_3$ (25 to 50 ml) to dissolve the deposit, the extract is concentrated by gentle distillation, made up to 50 ml, and a suitable aliquot (200 to 400 μg of Captan) is taken and (if necessary) reduced to ≃ 10 ml by passing a stream of dry air over its surface at 45° to 55° C. It is then passed through 0·5 g of Al_2O_3 (on cotton wool in a glass tube 5 to 6 mm in diam.) and washed with four successive 2-ml portions of $CHCl_3$. The percolate is collected in a boiling-tube, 0·3 g of resorcinol is added, and the mixture is evaporated to dryness in an air stream at 45° to 55° C. The tube is next heated in an oil bath for 15 min. at 135° C with occasional rotation and, before its contents solidify after removal from the bath, 10 ml of ethanol containing 10 per cent. v/v of 0·1 *N* aq. H_2SO_4 are added, the tube is stoppered, and allowed to stand for 1 hr. Any opalescence due to wax is filtered off and the extinction is measured with a Hilger Spekker photo-electric absorptiometer, with a 1-cm cell and violet filter No. 601. A standard curve is prepared with pure recryst. Captan. The concn. to extinction relationship is linear up to 600 μg of Captan. A series of determinations on strawberry, apple and pear fruits are reported. S.C.I. ABSTR.

591. **Fungicidal properties of coal-tar distillates: progress report II.** [**Analysis of tar-oil fungicides.**] G. V. Coles, J. T. Martin and R. J. W. Bryde (*Ann. Rep. Agric. Hort. Res. Sta., Bristol*, 1954, 74–82).—A sample (≃ 25 g, calculated on a water-free basis) of a tar-oil fungicide is distilled with benzene in a Dean and Stark apparatus to remove water and adjuvants (*e.g.*, emulsifiers and emulsion stabilisers), the latter being pptd. in the oil solution. The oil and solids are separated by continuous oil extraction, the flask containing the mixture being attached to a liquid extractor tube by a ground-glass cone inserted just below the side-arm. A perforated glass disc is fused to the lower edge of the cone and supports a cotton-wool filter pad. Through the central hole of the disc passes the extended stem of a filter-funnel. The oil in the mixture is washed over into a second flask by condensed benzene falling into the funnel. The solids remaining in the flask or on the filter pad are weighed. Acids and bases in the oil solution are separated by eight alkaline and five acid counter-current extractions by using benzene and, respectively, 5 per cent. w/w NaOH soln. and 5 per cent. w/w HCl. Phenols are recovered from the alkaline solution by passing CO_2 before recovering the other acids. Tar components are obtained by distillation, on a water bath, of most of the benzene, the remainder being removed by azeotropic distillation with methanol, followed by drying at 100° C for a short time. The fungicidal efficiencies of proprietary tar-oil fungicides and of constituent fractions were biologically assayed against *Ceratostomella fimbriata* and the results correlated with those of analysis carried out by the method described. The predominating effect of phenols in determining fungicidal efficiency was confirmed; no evidence was found of a synergistic effect between phenols and neutral oils.
S.C.I. ABSTR.

See also Abstract 615.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

592. **A modified Menzies - Wright ebulliometer for the semi-micro and micro-determination of molecular weight.** A. F. Colson (Imperial Chemical Industries Research Dept., Alkali Div., Northwich, Cheshire, England) (*Analyst*, 1955, **80**, 690–696).—An improved form of the Menzies - Wright ebulliometer, suitable for routine determinations of mol. wt. on the semi-micro or micro scale, is described, with detailed dimensioned diagrams of its components. The operation of the instrument is described and a series of results with a number of organic compounds in benzene or carbon tetrachloride as solvents are given. With ≃ 6 ml of solvent and 40 to 60 mg of sample the error in the determination of mol. wt. in the range 200 to 1000 does not exceed 3 per cent., and, if subsequent recovery of the sample is not desired, accuracy of the same order can be attained for mol. wt. of ≃ 200 with 10 to 15 mg of sample if a suitable amount of a non-reactive compound (*e.g.*, naphthalene) is added to the solvent. The apparatus is unsuitable for use with methanol, ethanol and toluene.
A. O. JONES

593. **A new device for micro-recrystallisations.** J. H. Cannon (Food and Drug Admin., St. Louis, Mo., U.S.A.) (*J. Ass. Off. Agric. Chem.*, 1955, **38** [3], 844).—In the apparatus described and illustrated, a bulb (≃ 4·5 ml capacity) is fitted with a 3-bulb air-condenser held by a spring. The bottom of the container bulb has an orifice 3 mm in diameter, in which is inserted a ground-in plug with a stem projecting above the rim of the container. An enlargement on the side of the bulb serves as a heating area. To dissolve the material in a solvent the apparatus is manipulated as a test-tube; after cooling, the condenser is removed and the crystallised material is released into a filter by manipulation of the stem of the stopper.
A. A. ELDRIDGE

594. **Laboratory stillhead.** F. T. Riley (Univ. Coll., Dublin, Eire) (*Chem. & Ind.*, 1955, [30], 940).—A stillhead for fractional distillation consists of a vertical tube, which acts as an air-cooled partial condenser; the top of the tube leads to a spiral condenser down which the vapour is condensed. The condensate is cooled and drawn off at a controlled rate by a capillary stopcock, surplus condensate being returned to a drip point at the lower end of the tube. A vent tube is also connected to the base of the spiral condenser. S.C.I. ABSTR.

595. **Valveless laboratory dispensing apparatus.** J. F. C. Tyler and R. E. Weston (Gov. Lab., Clement's Inn Passage, London) (*Chem. & Ind.*, 1955, [30], 940–941).—The apparatus consists of two identical all-glass syringes connected in series with a four-way stopcock which, when progressively rotated, alternately fills and discharges the syringes in turn to deliver successive measured quantities of liquid. S.C.I. ABSTR.

596. **Improvement of Koch micro-burette.** M. R. Verma and V. M. Bhuchar (Nat. Phys. Lab. of India, New Delhi, India) (*Chemist Analyst*, 1955, **44** [1], 26).—An improved Koch micro-burette is illustrated and described. It can be easily dis-

mantled for cleaning and is not readily broken in transit; broken parts can be easily replaced. Glass connection tubes and a finely drawn glass tip, which regulates the size of the drops delivered, are used. For ease of filling of the burette two holes, which are in alignment, are provided in the stopper and mouth-wall of the reservoir. For use with solutions containing volatile constituents, the reservoir can be closed by turning the stopper.

O. M. WHITTON

597. **Solubility of silicone stopcock-grease.** D. Taber (Dept. of Ind. Med., New York Univ. Postgrad. Med. Sch., New York, N.Y., U.S.A.) (*Chemist Analyst*, 1955, **44** [1], 26).—The solubility of silicones in ordinary organic solvents is sufficient to limit their utility when artefacts must be excluded. Thus, when 1·95 g of Dow - Corning silicone stopcock-grease was treated with light petroleum (boiling range 30° to 60° C) for 7 hr. in a Soxhlet apparatus, 1·72 g (88·2 per cent.) was extracted. Under the same conditions, acetone removed 0·80 g (43·5 per cent.) from 1·84 g of grease.

O. M. WHITTON

598. **Simple instrument for titrimetry without indicators. Gas-pressure end-point technique. IX. Iodometry, iodimetry, iodate and periodate titrimetry.** O. R. Gottlieb (Ornstein and Co., Rio de Janeiro, Brazil) (*Anal. Chim. Acta*, 1955, **13** [3], 214–221).—The apparatus and procedure for making gas-pressure end-point titrations (*Anal. Abstr.*, 1956, **3**, 286) is extended to titrations involving liberation of iodine from KI, reduction of iodine to HI, and oxidations with solutions of iodate and periodate (especially of coloured solutions obtained by treatment of certain organic compounds with HIO_4). Standard solutions of arsenite, iodine and hydrazine sulphate are used as titrants. The examples cited show that the precision and accuracy of the method are comparable with those for the usual visual end-point titrations.

W. J. BAKER

599. **Preparation of conductivity water.** S. Jacobs (Nat. Inst. Med. Res., Mill Hill, London, England) (*Chem. & Ind.*, 1955, [30], 944–946).—A simple apparatus for preparing conductivity water comprises a Pyrex-glass tube (length 75 cm, diam. 7·5 cm) containing a mixture (1:2) of the resins Amberlite IR-120 and IRA-400. The tube is connected at the base to a sintered-glass funnel, through which the eluate passes to a monitor conductivity cell to check water quality, and thence to a 5-litre Pyrex-glass reservoir. The resins are regenerated by separating the cation and anion beads in a mixture of alcohol and water.

S.C.I. ABSTR.

600. **Teflon barrier for paper chromatography.** E. Usdin (Inst. for Cancer Res., Philadelphia, Pa., U.S.A.) (*Chemist Analyst*, 1955, **44** [1], 27).—The use of Teflon resin dispersion as a solvent-proof barrier in paper chromatography is described. The barrier lines confine each unknown to one strip of paper. The dispersion is applied by a medicine dropper bent at 45° and having a capillary tip.

O. M. WHITTON

601. **A new detector for vapour-phase partition chromatography.** R. P. W. Scott (Nat. Benzole Co., Watford, Herts., England) (*Nature*, 1955, **176**, 793).—The two detectors most commonly used in vapour-phase chromatography are the vapour-density bridge (James and Martin, *Brit. Med. Bull.*, 1954, **10** [3], 170), which is very sensitive but difficult to manufacture, and the thermal conductivity cell (Ray, *J. Appl. Chem.*, 1954, **4**, 21), which is relatively simple to construct but lacks sensitivity. The detector developed by the author overcomes these disadvantages. It is readily constructed from easily available materials, is highly sensitive, with zero stability of 1 per cent. full-scale deflection, and enables quant. chromatograms to be obtained with 2-mg samples. It can be used with hydrogen or a gaseous mixture containing hydrogen as a carrier gas, and detection is based on measurement of the temp. of the flame when the exit gas is burned at a small jet. The presence of an organic vapour causes the flame to lengthen and engulf an Fe/Constantan or Pt/Pt + 14 per cent. Rh thermocouple enclosed in a draught-free container 2 mm above the jet. The thermocouple output is fed through a resistance network to a galvanometer or recorder. With a 4-ft. column of Celite impregnated with 18 per cent. of paraffin and a mixture of 75 per cent. of H and 25 per cent. of N as carrier, the column efficiency at 78° C was $\simeq$ 1000 theoretical plates and 4 μg of benzene gave 2 per cent. full-scale deflection. The detector is applicable to the quant. analysis of hydrocarbon mixtures, the area of any peak being directly proportional to the mass present, corrected for the heats of combustion of the substances, and is independent of the mass of the original charge. It is also suitable for a number of volatile oxy and chloro compounds.

K. A. PROCTOR

602. **Gas - liquid partition chromatography.** G. Dijkstra, J. G. Keppler and J. A. Schols (*Rec. Trav. Chim. Pays-Bas*, 1955, **74** [6], 805–812).—Gas - liquid partition chromatography is applied to the separation of aliphatic acids, esters, alcohols and aldehydes with 4 to 18 carbon atoms. The column is run at temp. between 80° and 230° C with stationary phases of silicone high-vacuum grease - Celite (10:1), or paraffin wax - Celite (10:2) (for the aldehydes only), and nitrogen gas is used as eluent at 1 atm. effluent pressure. The presence of the material to be separated is detected by difference in thermal conductivity of the effluent gas registered on a recorder. The rate of flow of gas through the column varies from 10 to 37 ml per min. The method is applied to the quant. analysis of esters and acids by measuring the area under the peak from the recorder, and this is best done by weighing rather than by planimetry. The minimum quantity of methyl propionate registered by the detector is 10 μg.

E. J. H. BIRCH

603. **Gas - liquid partition chromatography.** D. H. Lichtenfels, S. A. Fleck and F. H. Burow (Gulf Res. Dev. Co., Pittsburgh, Pa., U.S.A.) (*Anal. Chem.*, 1955, **27** [10], 1510–1513).—The use of gas - liquid partition chromatography for the analysis of complex hydrocarbon mixtures in the C_5 to C_8 range is described. Various liquid phases (dioctyl phthalate and Octoil–S on Celite 545) and various mobile phases (N, H and He) have been used on 10 to 14-ft. columns operated at 65° to 85° C. For an 18-component blend the average difference between observed and known concentrations was 7·7 per cent. of the amount present, and ranged from −15·5 to + 14·2 per cent.

K. A. PROCTOR

604. **Apparatus for the automatic analysis of alkali metals by ion-exchange chromatography.** V. Šimánek and J. Janák (Ústav pro naftový výzkum, Brno, Czechoslovakia) (*Chem. Listy*, 1954, **48** [11], 1623–1627).—An apparatus for the automatic determination of alkali metals by ion-exchange chromatography is described and illustrated. It consists essentially of a system of 2 columns (60 cm long and 12 mm in diam.) filled with a total of 35 g of the resin 'Extra-M,' and of a recording millivoltmeter, by means of which the variations in the electrical conductivity of the eluent liquid (0·2 *N* HCl) are continuously recorded; from the graph the amounts of alkali metals present in the sample (0·5 to 10 mg-equiv.) are evaluated. Sensitivity can be varied by means of suitable resistances.

G. GLASER

605. **Rotational viscometer for rapidly settling suspensions.** A. Bhattacharya and A. N. Roy (Indian Inst. Tech., Kharagpur, India) (*Anal. Chem.*, 1955, **27** [8], 1287–1290).—The design and calibration of a rotational viscometer which can be used to measure the apparent viscosity of a variety of materials, such as muds, sand slurries and fine coal suspensions in water, are described. The instrument is of the rotating-spindle type in which the outer cylinder is also free to move. The torque exerted on this outer cylinder sets it in motion, but this is simultaneously counteracted by a calibrated watch-spring which brings the cylinder to rest. Viscosity values are calculated from the degree of twist of this spring, and the working range of the apparatus can be modified to suit a particular fluid by using springs of appropriate stiffness. Modifications may be made to the viscometer to provide more sensitive and easier operation and temperature control. Provision is made for draining out the contents. K. A. PROCTOR

606. **A simple, high-sensitivity flame photometer.** G. Gergely and P. F. Váradi (*Magyar Kém. Foly.*, 1955, **61** [6], 182–189).—The apparatus consists of a glass-prism monochromator and an electron-multiplying photocell (RCA 931-A for Ca, Sr and Ba, and RCA 1-P-22 for K). The light-source is an oxygen - hydrogen flame, an atomiser similar to the Beckman type being used. The wavelengths used were 4226 A for Ca, 4607 A for Sr, and 4934 A for Ba. For each of these elements, a calibration curve was recorded at all three wavelengths, and from these the interference effects can be calculated; K is determined at 7660 and 7699 A. The limits of the determination are: Ca, 0·09 to 1770 μg per ml; Sr, 0·2 to 2065 μg per ml; Ba, 0·6 to 5900 μg per ml; K, 0·005 to 50 μg per ml. Problems connected with sensitivity are discussed. The method has been specially developed for the simultaneous determination of Ca, Sr and Ba in oxide-coated cathodes, and of K in K_2SiO_3. A. G. PETO

See also Abstract 504.

Optical

607. **The accuracy and precision of photo-electric spectrophotometers. Results of a collaborative test by the Dutch "Werkgroep Voor Photoelectrische Spectrophotometrie."** J. A. A. Ketelaar, J. Fahrenfort, C. Haas and G. A. Brinkman (Univ. Amsterdam) (*Photoelect. Spectr. Gr. Bull.*, 1955, [8], 176–179).—A collaborative test of optical density measurements of $K_2Cr_2O_7$ with 70 photo-electric spectrometers, carried out on similar lines to that organised by the British Photoelectric Spectrometry Group (Gridgeman, *Ibid.*, 1951, [4], 67), confirmed the British findings. Differences between instruments were found to exist so that a particular instrument always reads too high or too low, the standard deviation for this effect being ± 1·3 per cent. An important source of variation is in the manipulation of cuvettes, a standard deviation of ± 1·1 per cent. being found for this effect. Optical density estimates have an overall standard deviation of ± 1·7 per cent. and estimates on one instrument of the ratio of solution strength a standard deviation of ± 1·6 per cent. Beckman and Unicam instruments were found to be entirely equivalent. K. A. PROCTOR

608. **Electronically controlled spectrographic low-voltage spark, interrupted arc and d.c. arc source.** Á. Bardócz (Central Research Inst. Physics, Budapest, Hungary) (*Spectrochim. Acta*, 1955, **7** [4], 238–241).—This paper describes a source for variable-frequency electronically controlled low-voltage sparks, interrupted arcs and d.c. arcs, which is capable of producing direct and alternating polarity sparks and interrupted arcs, rectified sparks and arcs, and d.c. arcs. Ignition is provided by a new type of electronically controlled spark source, operated by a variable-frequency pulse generator, which also controls the charging circuit of the source. K. A. PROCTOR

609. **Absorption spectrophotometric micro-analysis in the ultra-violet region.** W. Hoppe (*Experientia*, 1955, **11** [7], 281–282).—A new instrument is described for u.v. spectrometry of microscopic preparations. It uses quartz objectives for magnification and monochromatisation and permits measurements up to extinctions of more than 2.

R. S. TONKS

610. **Hydrogen-lamp holder for DU Beckman spectrophotometer.** J. R. Edisbury and E. T. Sanders (Unilever Ltd., Port Sunlight, England) (*Photoelect. Spectr. Gr. Bull.*, 1955, [8], 187–188).—A modified lamp holder for the Beckman DU spectrophotometer is described. By using an all-quartz hydrogen lamp with an early model of the Beckman instrument it has regularly been found possible to reach below 210 mμ.

K. A. PROCTOR

611. **Quantitative application of potassium bromide disc technique in infra-red spectroscopy.** J. J. Kirkland (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.) (*Anal. Chem.*, 1955, **27** [10], 1537–1541).—A uniform small particle-size is the principal requirement in the preparation of samples for quantitative potassium bromide disc spectroscopy. An investigation of this variable has been undertaken with three methods of particle-size reduction and mixing with KBr, *i.e.*, ball-milling, grinding in a mortar and mechanical vibrator-grinding. The vibrator-grinding technique was found to be the best, particularly for preparing sample mixtures from difficultly ground materials; contamination by water is maintained at a low level with this technique. K. A. PROCTOR

612. **Small-sample infra-red spectrophotometry.** D. L. Wood (Univ. Michigan, Ann Arbor, Michigan, U.S.A.) (*Rev. Sci. Instrum.*, 1955, **26** [8], 787).—A device is described which can be attached to the

Perkin-Elmer model 21 double-beam spectrophotometer, and will mask the monochromator slit-height down to 3 mm. The device is located inside the instrument at the point where the two beams are superimposed, and is equipped with a solenoid selector-mechanism to permit selection of the short or full slit. A sample holder for the short slit is described. G. SKIRROW

613. **High-current mercury-arc Raman source.** E. R. Shull (*J. Opt. Soc. Amer.*, 1955, **45** [8], 670–671).—The mercury-arc lamp described has been designed to operate at sufficiently low vapour pressure to reduce spectral background to a minimum. Special attention to the cooling system has enabled the lamp to be operated at high current, thus achieving relatively high spectral-line intensity. The lamp is constructed of Pyrex glass with mercury-pool electrodes and a vertical discharge column. Each mercury pool is cooled by circulating cold (15° C) water through a "finger" extending through the mercury, whilst the arc column is cooled by circulating hot water (80° to 93° C) through a surrounding jacket. The normal operating current is 40 amp. with 47 V drop across the lamp, starting being performed with a high-frequency leak detector. With this lamp, for example, the spectrum of liquid CCl_4 can be obtained with an exposure of less than one minute using an 8-in. f/2 camera of the type described by Rank (*Brit. Abstr. C*, 1950, 505). B. S. COOPER

614. **An unusual instrumental error in photometric analysis.** D. F. Westneat, W. E. Keder and H. W. Safford (Univ. Pittsburgh, Pa., U.S.A.) (*Chemist Analyst*, 1955, **44** [1], 12–13).—The error found when light of low energy level strikes the photocells of the voltage-balancing circuit of a widely used U.S. photo-electric colorimeter is reported and discussed. It is traced to the illuminating pilot light which creates thermal potentials in the slidewire. O. M. WHITTON

615. **Use of fluorescence for the estimation of substances separated on paper by partition chromatography.** R. Mavrodineanu, W. W. Sanford and A. E. Hitchcock (*Contr. Boyce Thompson Inst.*, 1955, **18** [3], 167–172).—A modified Photovolt densitometer is described, in which the fluorescence produced by substances separated by paper partition chromatography, when irradiated with u.v. light, is used. A mercury-vapour lamp is used as a light source, with a filter inserted between it and the instrument aperture (0·5 cm in diam.), which allows the selected u.v. spectrum to fall on the paper, placed above the aperture. The transmitted light, after passing a second filter, reaches the photomultiplier tube connected to a micro-ammeter. The second filter eliminates most of the u.v. emission and is transparent to visible light. Different filters are used having max. transmissions at 465, 495, 515 and 570 mμ, selection being made according to the fluorescence characteristics of the substances under examination. The fluorescent material on the paper allows the excited emission radiation to be read off on the micro-ammeter. Measurements with an unknown substance isolated from tomato-plant extract, and with indol-3-ylacetic acid, showed a proportionality between the amount of material contained in the separated spots and the fluorescence produced. The lower limit of indol-3-ylacetic acid detected was about 0·5 μg per spot. G. R. WHALLEY

Electrical

616. **Paper electrophoresis with superimposed pH gradient.** H. Hoch and G. H. Barr (*Science*, 1955, **122** [3162], 243–244).—A pH gradient was established by wetting the horizontal paper strip (Whatman No. 3) from the side of the positive electrode with 0·05 *M* NaH_2PO_4 (pH 4·3) and from the other side with 0·01 *M* phosphate buffer of pH 7·4. The sample was then applied as a streak along the line where the two buffers met and 200 V were applied for 6·7 hr. Compared with the conventional method with barbitone buffer of pH 8·6 the bands showed a sharper separation with less trailing. An important feature of the pH-gradient technique is its concentrating effect during electrophoresis of dilute soln. It was found possible to obtain well-defined patterns with undiluted cerebrospinal fluids, containing 10 and 20 mg of protein per 100 ml, by using 0·8 ml of sample. Proteins such as haemoglobins A and F, whose iso-electric points differ little, cannot be separated by this technique.
H. F. W. KIRKPATRICK

617. **Electrophoretic separations on an inert supporting material. I, II.** R. Munier (*Chim. Anal.*, 1955, **37** [8], 253–263; [9], 283–300).—After a review of the principles and practice of electrophoresis, the following types of apparatus for making paper-electrophoretic separations are described and illustrated, their respective merits and limitations being indicated: (*i*) those based on evaporative cooling between 1° and 5° C, and specially suitable for determining electrophoretic mobilities or making separations with high potential gradients, (*ii*) those based on max. evaporation, and applicable to substances of high mol. wt. and low mobilities, and (*iii*) those based on controlled evaporation, and specially suitable for substances having very low or very high mobilities. The paper-electrophoretic separation of proteins is discussed in relation to the selection of electrophoretic buffer, the revealing of the separate bands and the analysis of the electrophoretic diagram obtained. Based on a review of the literature, optimum operating conditions for the electrophoretic separation of, *e.g.*, sera, plasma, egg albumin, enzymes, alkaloids, hormones, peptides, vitamin phosphates and nucleic-acid derivatives, are tabulated. The separation of amino acids or proteins by two-dimensional paper electrophoresis is described, as well as devices and operating conditions for successful continuous paper electrophoresis.
W. J. BAKER

618. **A simple automatic recorder for electrometric titrations.** K. Engelthaler (Ústav pro technologii hrubé keramiky, Horní Bříza, Czechoslovakia) (*Chem. Listy*, 1954, **48** [10], 1572–1573).—A simple procedure is described for the determination of the amount of reagent consumed in an electrometric titration. The reagent is added to the titrated soln. through a capillary at a constant rate, and the weak electrode currents are recorded on a rotating polarographic drum. The length of the recorded curve is proportional to the titration time and therefore to the quantity of reagent added.
G. GLASER

619. **High-frequency titrations. XIII. Studies on concentration curves by a capacitance-type instrument.** Ynichi Kamura (Pharm. Inst., Univ.

Tokyo) (*Pharm. Bull., Japan*, 1955, **3** [2], 138–143).—The theoretical approach to methods of high-frequency analysis has been studied and it is pointed out that it is necessary to relate this to the actual method of measurement used. High-frequency energy of constant frequency and power was applied to solutions both directly, by immersing the electrodes, and indirectly through the walls of the containing vessel. In each case, measurements were made on a bridge and correlation sought between the two sets of readings. With the results thus obtained, a formula was derived which could be applied to currently employed apparatus for high-frequency analysis. A number of curves are presented showing the similarity between those plotted from experimental results and those predicted by theory.

J. ALLEN

620. **Use of oscillographic polarography in quantitative analysis. II. An electronic switch.** R. Kalvoda, O. Mach and J. Doležal (Ústav pro chem. anal. Karlovy Univ., Prague, Czechoslovakia) (*Chem. Listy*, 1954, **48** [11], 1688–1689).—The circuit and construction of an electronic switch with a multivibrator, suitable for use in oscillographic polarography, are described. G. GLASER

621. **Nuclear magnetic resonance spectroscopy.** R. Velasco (Inst. de Opt., "Daza de Valdés," Madrid, Spain) (*Inf. Quím. Anal.*, 1955, **9** [3], 95–102).—General principles, apparatus, scope and sensitivity of nuclear magnetic resonance spectroscopy are discussed. L. A. O'NEILL

622. **Some new technical and chemical applications of the radio-frequency mass spectrometer. II. The utilisation of the RF mass spectrometer for the qualitative and quantitative analysis of gases.** P. F. Váradi and G. L. Sebestyén (*Magyar Kém. Foly.*, 1955, **61** [6], 176–182).—The effect of various parameters on the resolution and sensitivity of the previously described mass spectrometer (*Anal. Abstr.*, 1955, **2**, 3554) is discussed. At 10^{-4} to 10^{-6} mm, with a mass-resolution of 20, a 1 per cent. component in the gas mixture could be detected. At 10^{-3} to 10^{-7} mm of Hg, the relation between gas pressure and ion-current is linear, but the mass-scale must be calibrated with a known gas. The apparatus has been used for gas analysis during the degassing of radio valves and also for determining the gas-releasing properties of vacuum-tube components.

A. G. PETO

623. **Heated sample-inlet system for mass spectrometry.** V. J. Caldecourt (The Dow Chem. Co., Midland, Mich., U.S.A.) (*Anal. Chem.*, 1955, **27** [10], 1670).—A heated sample-inlet system has been developed for convenient loading of weighed amounts of liquids or solids for mass spectrometry. The solids may be volatile at the temp. of the reservoir or non-volatile materials containing volatile components. The system is constructed of Teflon, glass and stainless steel and can be used up to about 250° C. The chief limitation is the introduction of a small amount of air into the system during loading, *e.g.*, about 0·003 mg of air is introduced with 7 mg of toluene, but few samples react with air at the temp. used. K. A. PROCTOR

624. **Continuously recording oxidation apparatus for hydrocarbon oils.** D. G. Childs (Central Electr. Auth., London, England) (*J. Inst. Petrol.*, 1955, **41**, 283–289).—The apparatus described is entirely constructed of Pyrex glass with standard ground-glass joints. The oil sample is contained in a 250-ml conical flask maintained at the required temp. in an oil-bath. An all-glass, double-acting magnetic pump passes O through the sample, after which the gas rises through a Liebig condenser and passes back to the circulating system through silica gel backed with $Mg(ClO_4)_2$ to remove water, and soda asbestos to remove CO_2. The oxygen-circulating system is a monostat constant-pressure system connected to a gas burette containing dibutyl phthalate, the level of which is continuously recorded photo-electrically by the intermittent interruption of a light-beam by an opaque float on the liquid surface. The apparatus can be used both for assessing the inherent oxidation stability of insulating oil and for evaluating antioxidants.

S.C.I. ABSTR.

See also Abstracts 333, 344.

ERRATUM.—January (1956) issue, abstract 245, third line from bottom. Delete "more" after "$\simeq$".

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångstrom unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher -e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
critical	crit.
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c.p.s.
decompos -ing, -ition	(decomp.)
density	ρ
density, relative	d or wt. per ml
derivative	deriv.
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
electron-volt	eV
equivalent	equiv.
experiment	expt.
foot, feet	ft.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
horse-power	h.p.
hour	hr.
hydrogen ion concentration	$[H^{\cdot}]$
hydrogen ion exponent	pH
inch	in.
infra-red	i.r.
insoluble	insol.
kilogram	kg
kilovolt	kV
kilowatt	kW
maxim -um, -a	max.
melting-point	m.p.
microcurie	μC
microgram	μg
microlitre	μl
micron	μ
milliampere	mA
millicurie	mC
milligram	mg
millilitre	ml
millimetre	mm
millimicron	mμ
millivolt	mV
minimum	min.
minute (time)	min.
molar (concentration)	M
molecul -e, -ar	mol.
normal (concentration)	N
number	no.
observed	(obs.)
ounce	oz
part	pt.
patent	pat.
parts per million	p.p.m.
per cent. wt. in wt.	per cent. w/w
per cent. wt. in vol.	per cent. w/v
per cent. vol. in vol.	per cent. v/v
potential difference	p.d.
pound	lb
precipitate	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n
relative humidity	R.H.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]$
square centimetre	sq. cm
standard temperature and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition the following symbols are used—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, *e.g.*, $Cu^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, Cl', SO_4''. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, *e.g.*, ferric iron becomes Fe^{III} and cuprous copper Cu^{I}.

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